LOW SURFACE ADHESION HDPE/PTFE BLENDS

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พอลิเอทิลีนและพอลิเตตระฟลูออโรเอทิลีนผสมที่มีค่าการยึดเกาะผิวต่ำ

นายนันทวุฒิ จันทนากร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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LOW SURFACE ADHESION HDPE/PTFE BLENDS

Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master’s Degree.

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นันทวุฒิ จันทนากร : พอลิเอทิลีนและพอลิเตตระฟลูออโรเอทิลีนผสมที่มีค่าการยึดเกาะผิวต่ำ (LOW SURFACE ADHESION HDPE/PTFE BLENDS) อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.อุทัย มีคำ, 303 หน้า.

จุดประสงค์ของวิทยานิพนธ์นี้เพื่อศึกษาสูตรการผสมระหว่างพอลิเอทิลีนความหนาแน่นสูง พอลิเตตระฟลูออโรเอทิลีน พอลิเอทิลีนน้ำหนักโมเลกุลสูง และสารตัวเติมชนิดต่างๆ โดยใช้ไดคิวมิวเปอร์ออกไซด์และไซเลนในระบบการเกิดโครงสร้างร่างแหของสายโซ่โมเลกุลของพอลิเมอร์ผสมระหว่างพอลิเอทิลีนความหนาแน่นสูงกับพอลิเตตระฟลูออโรเอทิลีน ซึ่งมีเป้าหมายคือการนำพอลิเอทิลีนและพอลิเตตระฟลูออโรเอทิลีนผสมที่มีค่าการยึดเกาะผิวต่ำนี้ไปใช้ในการเก็บเกี่ยวน้ำยางธรรมชาติ พอลิเมอร์ผสมนี้ถูกเตรียมด้วยเครื่องอัดรีดแบบสกรูคู่ ชิ้นทดสอบถูกเตรียมด้วยเครื่องฉีดขึ้นรูปและทดสอบตามวิธีการมาตรฐาน วิธีการเชิงสถิติแบบการทดลองแบบพหุคูณ (2^K) ถูกนำมาใช้เป็นเครื่องมือในการวิเคราะห์ผลของตัวแปรต่างๆ จากการวิเคราะห์ทางสถิติพบว่าไดคิวมิวเปอร์ออกไซด์และปฏิสัมพันธ์ระหว่างพอลิเตตระฟลูออโรเอทิลีนและไซเลนมีผลกระทบในทางลบต่อดัชนีการไหลของพอลิเมอร์ผสมระหว่างพอลิเอทิลีนชนิดความหนาแน่นสูงและพอลิเตตระฟลูออโรเอทิลีน ในขณะที่ปริมาณของไดคิวมิวเปอร์ออกไซด์ยังมีอิทธิพลเชิงลบต่อสมบัติความต้านทานการดัดงอของวัสดุชนิดนี้ก่อนถูกอบ

จากการศึกษาเพิ่มเติมได้ข้อสรุปว่าอุณหภูมิการโก่งงอลดลงของพอลิเมอร์ผสมก่อนถูกอบนี้ลดลงเมื่อเพิ่มอัตราส่วนของไซเลนในระบบโครงสร้างร่างแหแต่หลังจากทำการอบชิ้นงานทำให้อุณหภูมิการโก่งงอเพิ่มขึ้นเล็กน้อย พอลิเมอร์ผสมระหว่างพอลิเอทิลีนความหนาแน่นสูงและพอลิเตตระฟลูออโรเอทิลีนกลายเป็นวัสดุที่มีความยืดหยุ่นมากขึ้นเมื่อเพิ่มปริมาณของไซเลน ซึ่งสามารถสังเกตุได้จากสมบัติความต้านทานการดัดงอ ความต้านทานต่อแรงดึงและความต้านทานต่อแรงกระแทกของวัสดุดังกล่าว ด้วยเหตุนี้จึงส่งผลให้ความต้านทานการสึกหรอดีขึ้น การปรับปรุงพื้นผิวของพอลิเตตระฟลูออโรเอทิลีนโดยไดคิวมิวเปอร์ออกไซด์ก่อนทำการผสมกับพอลิเอทิลีนชนิดความหนาแน่นสูง แสดงให้เห็นว่าอุณหภูมิที่ใช้ในการแตกตัวของไดคิวมิวเปอร์ออกไซด์ไม่มีผลต่อสมบัติเชิงกลของพอลิเมอร์ผสมระหว่างพอลิเอทิลีนความหนาแน่นสูงกับพอลิเตตระฟลูออโรเอทิลีน อย่างไรก็ตามสามารถสังเกตเห็นได้ว่าการยึดติดกันระหว่างพอลิเอทิลีนความหนาแน่นสูงกับพอลิเตตระฟลูออโรเอทิลีนที่ถูกปรับปรุงพื้นผิวนั้นดีขึ้น จากการผสมพอลิเอทิลีนน้ำหนักโมเลกุลสูงลงในพอลิเมอร์ผสมระหว่างพอลิเอทิลีนความหนาแน่นสูงและพอลิเตตระฟลูออโรเอทิลีนถูกพิจารณาเมื่อผสมพอลิเอทิลีนน้ำหนักโมเลกุลสูงในอัตราส่วนที่มากกว่า 5 ต่อ 100 ส่วน ซึ่งทำให้สมบัติเชิงกลลดลงเมื่อเพิ่มปริมาณของพอลิเอทิลีนน้ำหนักโมเลกุลสูง อย่างไรก็ตามสมบัติการ

ต้านทานต่อแรงกระแทกของวัสดุกลับเพิ่มขึ้นเมื่อเพิ่มปริมาณของพอลิเอทิลีนน้ำหนักโมเลกุลสูง นอกจากนี้การศึกษาผลของอุณหภูมิการเตรียมพอลิเอทิลีนน้ำหนักโมเลกุลสูงโดยผสมกับพอลิเอทิลีนความหนาแน่นสูงก่อนที่จะทำการผสมกับพอลิเมอร์ผสมระหว่างพอลิเอทิลีนความหนาแน่นสูงและพอลิเตตระฟลูออโรเอทิลีน สังเกตเห็นได้ว่าพอลิเอทิลีนน้ำหนักโมเลกุลสูงสามารถกระจายตัวในเนื้อของพอลิเมอร์ผสมนี้ได้ดีขึ้น แต่อุณหภูมิที่ใช้ในการเตรียมไม่มีผลต่อคุณสมบัติของพอลิเมอร์ผสมนี้แต่อย่างใด

ผงอิฐทนไฟและผงอิฐทนไฟผสมทาล์คัมถูกนำมาใช้ในพอลิเมอร์ผสม พอลิเมอร์ผสมที่มีการใส่อิฐทนไฟมีค่าดัชนีการไหลที่เพิ่มขึ้นเมื่อเพิ่มปริมาณของอิฐทนไฟ เช่นเดียวกับสมบัติเชิงกลและสมบัติทางความร้อนนั้นสูงขึ้นเมื่อปริมาณของอิฐทนไฟเพิ่มขึ้น การใช้สารตัวเติมร่วมกันระหว่างอิฐทนไฟกับทาล์คัมในพอลิเมอร์ผสมนี้พบว่า สมบัติเชิงกลลดลงเมื่อเพิ่มอัตราส่วนของผงอิฐทนไฟ แต่ทำให้ความต้านทานต่อแรงกระแทกเพิ่มขึ้น จากการศึกษาแรงที่ใช้ในแยกการยึดติดของพื้นผิวพอลิเมอร์ผสม พบว่า แรงที่ใช้ในแยกการยึดติดต่ำลงเมื่อทำการผสมสารตัวเติมระหว่างอิฐทนไฟและทาล์คัมในอัตราส่วน 20 ต่อ 30 ลงในพอลิเมอร์ผสมนี้

สาขาวิชา วิศวกรรมพอลิเมอร์ ลายมือชื่อนักศึกษา____________________
ปีการศึกษา 2556 ลายมือชื่ออาจารย์ที่ปรึกษา______________

NUNTAWUT CHANTANAKORN : LOW SURFACE ADHESION HDPE/PTFE BLENDS. THESIS ADVISOR : ASST. PROF. UTAI MEEKUM, Ph.D., 303 PP.

SURFACE ADHESION/HDPE/PTFE/UHMWPE/CROSSLINK/2^K FACTORIAL DESIGN OF EXPERIMENT/SURFACE TENSION

This thesis aimed to study the compounding formula between HDPE, PTFE, UHMWPE and filler(s). DCP and silane were used as macro chain crosslink system in the HDPE/PTFE blend. The low surface adhesion HDPE/PTFE applied for non-stick rubber latex harvesting container was targeted. The polymer compound was performed in the closely intermeshing co-rotating twin screw extruder. The test specimen was prepared by injection molding and tested according to the standard methods. The 2^k factorial design of experiment (DOE) as primary tool to determine the effect the blend constituents reviewed that the DCP and interaction amount between PTFE and silane content used in the HDPE/PTFE blending had negatively and significantly affected to MFI of the blend. While, DCP content was negative and significant effect to the flexural strength of the sample without sauna curing.

Later studies concluded that the HDT of the original samples was decreased with increasing the ratio of silane in the crosslink system but the HDT was slightly increased with increasing the silane after undergoing the sauna treatment. The HDPE/PTFE became more flexible material, or softer, when increasing in the silane fraction. It was indicated by the flexural, tensile and impact properties. Therefore, the superior in the wear of the samples was found. The surface treatment of PTFE by

DCP before blending with HDPE, the results suggested that decomposition temperatures of DCP during the treatment did not have the significant effect on the mechanical properties of HDPE/PTFE blend. However, better in the interfacial adhesion between HDPE matrix and treated PTFE were observed. Addition of UHMWPE as toughener into the HDPE/PTFE blend was verified at UHMWPE content above 5 phr. The mechanical properties were decreased with increasing the UHMWPE contents. However, the impact strength was increased with increasing the UHMWPE portion. The effect of HDPE/UHMWPE master batching temperatures before compounding with HDPE/PTFE was resolved. It was manifested that better dispersion of UHMWPE in the blend was obtained when the UHMWPE/HDPE master batch pellet was used. The master batching temperatures had no significant effect on properties of final HDPE/PTFE/UHMWPE compounds. The fire clay powder and the combined talc/fire clay fillers were added into the HDPE compound. The compound filled with fire clay showed that the MFI of the HDPE/PTFE/UHMWPE compound was increased by adding fire clay. The mechanical and thermal properties of the composite material were slightly increased with increasing the fire clay loading. For the combined fillers, talc/fire clay, it was observed that the mechanical properties were also slightly inferior when high portion of fire clay fillers was added. The impact was slightly increased with increasing the fire clay fraction. Peeling force investigation on the surface of the compound was conducted. It was evidenced that the lower peeling force was obtained while adding low polarity fillers, 30 to 20 of talc and fire clay, onto the polymer blend.

School of Polymer Engineering Student’s Signature______________

Academic Year 2013 Advisor’s Signature______________

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SYMBOLS AND ABBREVIATIONS

% = Percent

^{o}C = Degree Celsius

μm = Micrometer

g = Gram

g/cc = Grams per centimetre cubed

g/cm^{3} = Gram per cubic centimeter

GPa = Gigapascal

hr = Hour

J = Joule

J/m = Joule per mater

keV = Kilo electron volt

kg = Kilogram

kGy = Kilogray

kJ = Kilojoule

kJ/m^{2} = Kilojoule pers quaremeter

SYMBOLS AND ABBREVIATIONS (Continued)

kN = Kilonewton

mm = Milliliter

mm/min = Milliliter per Minute

min = Minute

m^2/g = Square meter per gram

MPa = Megapascal

Phr = Part per hundred resin

Rpm = Revolution per minute

w/w = Weight by weight

wt% = Percent by weight

CHAPTER I

INTRODUCTION

1.1 General introduction

Today, Asia is the main source of natural rubber supplier, accounting for around 94% of the total output in 2005. Especially, Thailand has been the largest exporter of natural rubber for decade. In the past, the half of coconut shell was used as the harvest container for the rubber latex. Recently, ceramic pottery and plastic cups are the main latex container. The cups are supported by a wire that encircles the tree. This wire incorporates a spring, so it can stretch as the tree grows. The latex is led into the cup by a galvanized "spout" knocked into the bark. Tapping normally takes place early in the morning, when the internal pressure of the tree is highest. A good tapper can tap a tree in every 20 seconds on a standard half spiral system.

Some trees will continue to drip into the cup after finishing the collection and this leads to a small amount of cup lump which is collected at the next tapping. The latex that coagulates on the cut is also collected as tree lace. Tree lace and cup lump together account for 10–20% of the dry rubber produced. The latex will coagulate in cup if it is kept for long period of time. The latex has to be collected before coagulation. The collected latex is transferred in to coagulation tanks for the preparation of dry rubber in form of standard crepe or bale. They are normally treated as premium grade of natural rubber. Naturally, the coagulated rubber (cup lump) is also used as low price and second grade of rubber by some manufacturers. The processing of the latex rubber is basically a size reduction and cleaning process to remove contamination and prepare the material for the final stage of drying.

Cups are a very important for harvesting rubber latex. When thinking of planting areas around the country in Thailand, about 5 million hectares. By gardener rubber is planted with approximately 70 trees per hectare. The total planted trees require over 850 billion cups for harvesting the latex. The cups are made from ceramic pottery that quite heavy and easily to be broken. It is likely to cost more, because the manufacturing process uses more energy. The cups that made from plastic such as polyvinylchloride (PVC) and high density polyethylene (HDPE), there are normally cheaper, approx. 3 baths per cup. But as they are light weight, therefore they are easily blown away by the wind while hanging with the rubber. It becomes a waste, pollution affect the environment in the rubber plantations. Moreover, the accumulated dried rubber is normally deposited on the cup both pottery and plastics. It is routinely removed by mechanical peeling from time to time and sold as cup lump with cheaper price. As the crude oil price has gone up and there is sign of future depletion, consequently price of natural rubber crepe and bale has been hurdled to more than 4$ per kilogram (quoted as 2012). It would much benefit for the rubber cultivators if ones can reduce the cup lump and cup cleaning up time.

In this thesis work, compounding of PTFE with HDPE in order to incorporate excellent surface properties of PTFE into the lower cost HDPE to produce material for manufacturing the non stick, lump free, rubber cup and others related benefit is the main research goal. The compounding techniques both chemically and polymer technology to assist the good adhesion between PTFE and HDPE will be explored.

1.2 Tribology in Polymeric Materials

The tribology of polymers is different from tribology of metals and ceramic materials. The difference of application of polymers in frictional contacts in comparison to metals and ceramic materials relates mainly to the chemical and physical structures as well as to the surface and bulk properties. The polymers show very low surface free energy and also have the viscoelastic properties. It effects in drastic tribological differences when adhesive and mechanical components of friction force were considered. Also polymers can be easily modified both on surface and in bulk. Therefore there are often and easily used as a background material to produce many composites with easily varied physicochemical properties. Tribology in polymeric material had been defined in three studies.

Friction is the resistance to motion that occurs whenever one solid body is in contact with another solid body. It can be defined as the tangential resistance force (F) in the relative motion of two surfaces in contact

$$F = \mu.\mathrm{N} \tag{1.1}$$

Where N is the normal force and μ represents friction coefficient. Eq. (1.1), thus, friction represents the tangential drag force acting in direction directly opposite to the direction of motion. According to Eq. (1.1), the friction resistance is proportional to the load (N) and μ is independent of the apparent area of contact between the bodies. The parameter μ is often called "friction coefficient”.

Wear represents a surface damage or removal of material from one or both sides of solid surfaces that are in contact during motion. Wear of a material can be mechanical and/or chemical; it is generally accelerated by heating during friction. Wear mechanism can be adhesion, abrasion, fatigue, and the effect of erosion, chemical reactions including corrosion, or else an induced electric arc. The main wear mechanism is adhesion, which is an important component of friction. Adhesive wear process involves creation of adhesive bonds, their growth and breaking when the material is transferred from one surface to another15. It is important to note that wear is usually not the result of a single mechanism but a combination of different mechanisms. Wear is most often defined as the unwanted loss of solid material from the solid surface caused by mechanical interactions3. Then wear is quantified by determination of the specific rate of wear μ_{sp} by measuring the volumetric loss of the sample, V_{loss}, with the applied force, F, and the length of sliding, D.

$$\mu_{sp} = \frac{V_{loss}}{F.D} \tag{1.2}$$

According to Eq. (1.2), wear is determined from the volume (or mass) of fragments, or wear products that are separated from the specimen during the wear.

Lubrication is very significant in tribological behavior of both non-polymer-on-polymer and polymer-on-polymer contacts. Friction and wear behaviors can be improved as well as friction and wear rate can also increase in the effect of lubrication. It mainly depends on interactions between polymer and lubricant. The adsorption and even absorption of lubricant by polymer can effects in the plasticization of the surface layer and even of bulk polymer. Polymeric tribosystems can operate without lubrication. Very wide possibilities to modify polymeric materials by fillers, lubricants and many other additives give very good perspectives to find polymeric composites that show excellent tribological properties both as matched with non-polymer or with another polymeric component. The lubrication enhanced these possibilities when the lubricant is optimized. The construction of self-lubricating tribosystems is much easier to realize than in ceramic or metallic sliding or rolling contacts. Nowadays in technology polymers are seen as the most important future materials. The study shows that polymers as tribological materials are very good for low cost rubbing components in machines and devices.

1.3 Research objectives

The main objectives of this research in order to obtain the polymer compound that is suitable for manufacturing the non stick rubber cup include;

(1) To study the compounding formula between PTFE and HDPE.

(2) To study the effect of filler on the properties of PTFE and HDPE Blends.

1.4 Scope and Limitation of the Study

In this work, the blend between HDPE, PTFE, UHMWPE and filler(s) were explored. DCP and silane were used as macro chain crosslink system. The compound was performed in the closely intermeshing co-rotating twin screw extruder having the screw diameter of 25 mm, L/D ratio of 20 and equipped with three quartet kneader disk. The test specimen of compound obtained was prepared by injection molding. The statistical approach namely 2^k factorial design of experiment (DOE) was preliminary explored to resolve the optimal compound ingredient especially the amount of macro crosslink reagents and matrix ingredients. The mechanical testing by mean of impact strengths, flexural and tensile properties were measured and used for discussion and conclusion. Also, the compound surface evaluation; abrasion testing and surface tension by the modified test method, were examined. The morphology of the prepared compound was also investigated by scanning electron microscopy (SEM). Finally, actual surface adhesion strength between dried natural rubbers with the HDPE/PTFE based compound by peeling test was reported.

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CHAPTER II

RITERATURE REVIEW

2.1 PTFE in Polymer Blends

D. L. Burris and W. Gregory Sawyer (2006) presented a PEEK filled PTFE composite that exhibited low friction and ultra low wear. It was hypothesized that a synergistic effect shuts down the dominant wear mechanism of each constituent. The friction coefficient and wear rate of this composite material on lapped stainless steel were evaluated for samples with PEEK wt. % of 0, 5, 10, 20, 30, 40, 50, 70 and 100 using a linear reciprocating tribometer. Tests were performed in filtered, standard laboratory conditions. The friction coefficients, averaged over an entire test, ranged from friction coefficient = 0.111 for a 50% wt. composite to friction coefficient = 0.363 for unfilled PEEK. Wear rates ranged from K= 2.3×10^{-9} mm^3/ (Nm) for a 20 wt. %PEEK sample to K=6×10^{-4} mm^3/ (Nm) for unfilled PTFE.

J. Bijwe (2005) reported the influence of increasing amounts of PTFE in the PEEK/PTFE blends on abrasive wear behavior along with a correlation with strength properties. In the work, five injection molded blends of PEEK with PTFE in the range of 0 to 30 wt. % were evaluated on a pin-on-disc configuration tester for their tribobehavior in the low amplitude oscillating wear mode. It was found that with an increase in PTFE contents, coefficient of friction in both the wear modes (adhesive and low amplitude oscillating) decreased but the trends in wear performance differed. In the adhesive wear mode, the specific wear rate showed minima for 7.5% PTFE inclusion followed by a slow increase for further PTFE addition. On the other hand, the wear rate continuously decreased for the selected compositions. The 30% PTFE blend showed excellent combination of friction coefficient and wear rate. Unfilled PEEK proved to be fairly good wear resistant material but exhibited high friction coefficient. Abrasive wear performance of the blends, on the other hand, deteriorated with increasing amount of PTFE.

J. Xie (2010) investigated the tribological behavior of PEEK and PTFE composites reinforced with potassium titanate whiskers (PTW). It was found that the PTW reinforced PEEK/PTFE composites exhibited much better tribological properties than those without PTW. Both the friction coefficient and the wear rate decreased with the increase of the PTW content. The crystallinity of the composite measured from differential scanning calorimeter slightly decreased with the addition of PTW, which might imply that the crystallinity of PEEK was not the dominant factor that influenced the tribological properties of the composites.

P. S. Thomas and B. H. Stuart (2003) observed PEEK/PTFE blends by using differential scanning calorimetry and wide angle X-ray crystallography. The observed changes in morphology were rationalized in terms of a higher degree of order imparted on the PEEK crystalline phase by the transmission of an applied .hydrostatic pressure by the presence of the PTFE. A pressure induced increase in the order of the crystalline lamellae in PEEK had been observed in the presence of PTFE and had been substantiated by both DSC and WAXD measurements. As noted, it was, in the composition range of 10 to 15% wt., that the transition in physical properties occurred. This study had noted a significant change in the morphology above and below the critical composition. It was possible that the change in properties was associated with the change in crystallinity. They suggested that a closer inspection of these effects on the composition around the critical compositional range is required and will be the subject for further characterization of the morphology of PEEK.PTFE blends.

The use of PTFE/PU membrane for chemical protective clothing was discussed by X. Hao, J. Zhang and Y. Guo (2004). By means of texturing with organic conductive fiber, and then treating with JAM-Y1, anti-bacteria agent, in the end, treating with the XL-550, waterproof agent, the PET fabric became permanent anti-static, anti-bacteria and waterproof and anti-oil properties. The PTFE/PU protective material was prepared by laminating with PET fabric by paste dot coating, and then coated by PU solution in a direct process. The PU coating agent, DMF and acetone, were used in testing through surface tension and peeling strength measurement. The penetration property of poliomyelitis virus in liquid and animalcule in air of PTFE membrane laminated textile, after being coated by PU solution were measured. The results show that it can separate SARS virus in air and liquid, and WVT was 11,496 g/24 hm^2. Then, it provided a satisfactory wearing comfort.

Z. Rong-guo et al., (2006) studied effects of PTFE content on water absorptivity, tensile strength, flexural strength and notched impact strength of PTFE/PA6 and PTFE/PA66 blends. It was investigated by water immersion test, uniaxial tensile test, three-point test, and Charpy impact fracture test. The water absorptivity in the blend decreased with increasing PTFE content, which indicated that the PTFE phase restrained the polyamide phase from water absorption. For water free blends, the addition of PTFE caused a reduction in tensile strength, while for water absorbed PTFE/PA6 blends, the tensile strength increased with increasing

PTFE. Simultaneously, the absorbed water improved the elongation, but resulted in a notable reduction in flexural strength of the blends. Although the addition of PTFE caused a reduction in notched impact strength of the blends, as compared to pure polyamide, the absorbed water had little effects on the notched impact strength of the blends. Finally, the effects of temperature and loading frequency on complex viscosity parameters of PTFE/PA6 and PTFEPA66 melts were tested. It was found that the complex viscosity of PTFE/PA6 melt was reversed with increasing temperature and shear velocity, but that of PTFE/PA66 melt increased approximately in exponential form with increasing temperature. To fill polyamide with suitable mass percentage of PTFE can effectively reduce the viscosity of blend, and as a result, the molding and processing properties were improved.

In M. Teoh, T. Chung and Y.S. Yeo (2011) work, the PVDF/PTFE composite was used to fabricate hollow fiber membranes for seawater desalination via direct contact membrane distillation application. The incorporation of PTFE particles in the formulated dope solution efficiently suppressed the formation of macro voids and enhanced the outer surface hydrophobicity. Dual layer hollow fibers with a desirable macro void free morphology and a relatively thin (13±2 µm) outer layer were obtained via blending 30% wt of PTFE particles in the outer layer dope. The resultant, dual layer hollow fiber (DL-30), displayed a moderately high contact angle of 114.5◦ and porosity of 81.5% wt. compared to the single layer hollow fiber with 30% wt (SL-30) PFTE particles. The DL-30 fiber exhibited a flux enhancement of approximately 24% that was contributed to the reduction in inner layer mass transfer resistance. Dual layer membrane configuration with a lower wall thickness as well as larger outer and inner diameters provided even higher water vapor transport was potentially suitable for desalination. Both single and dual layer PVDF/PTFE hollow fiber membranes revealed good long-term stability of up to 100 hours of continuous testing. By utilizing the state-of-the-art dual layer spinning technology, hollow fiber membranes with better performance (i.e. enhanced flux) and morphology (i.e. macro void free) cold be tailored.

C. Martini et al.,(2010) presented the influence of PEO treatments on the tribological behaviour of the Ti–6Al–4V dry sliding against the EN100Cr_6 steel. Three different sets of coatings were produced; (set 1) in an aluminate-rich electrolyte; (set 2) in a phosphate-rich electrolyte; and (set 3) identical to set 2, but with the addition of a spray deposited PTFE topcoat. The topography, microstructure, phase constitution and surface micro hardness of each set were characterized and dry sliding tests were carried out in the load range 5 – 120N using a block on ring tribometer. For each set, a transition load which corresponds to the end of coating life was identified. The highest transition loads were observed for coatings produced using the aluminate-rich electrolyte (set 1). Intermediate values of transition load were measured for duplex PTFE/PEO coatings (set 3). Single-layer PEO coatings produced in the phosphate-rich electrolyte (set 2) showed the lowest values of transition load, due to the low coating thickness and poor uniformity. The deposition of the PTFE topcoat proved to be beneficial in terms of both friction and wear resistance, particularly in an intermediate, 30 – 50 N, load range

2.2 UHMWPE and Polymer Blends

2.2.1 UHMWPE in polymer blends

C.Z. Liu et al., (2002) studied on an orthogonal test design and analysis method. The lubricated wear performance of PA-6/UHMWPE alloys was studied by using a pin-on-disc method. The effects of several parameters on the wear of the PA-6/UHMWPE alloy, rubbing against a stainless steel counterface, were reported. The main purpose was to study the influence of parameters such as sliding distance, counterface surface roughness, load and sliding speed, as well as their interactions on the wear performance. Statistical analysis was carried out to develop an equation, in which the wear volume of the polymeric specimen was expressed in terms of the investigated parameters. It was observed that the pressure and surface roughness were the two important and controlling factors; sliding distance and sliding speed had a minor effect on the wear of the specimens. Although the two-factor and three-factor interactions had little effect, the four-factor interaction had a strong effect on the wear of specimens. The results gave a comprehensive insight into the rear of the PA-6/UHMWPE alloy.

UHMWPE filled epoxy gradient composites has been developed by N. Chand, U.K. Dwivedi and M.K. SharmaI (2007). Samples were prepared for different centrifugation time periods. SEM and optical microstructures confirmed the graded dispersion of UHMWPE particles in the epoxy matrix. Quick estimation of gradient characteristics was done by abrasive wear measurements. Sliding wear tests were conducted by using a pin-on-disc machine. The sliding wear rate of composites reduced on increasing centrifugation time. Reduction in sliding wear rate in

UHMWPE filled epoxy gradient composites was attributed to the reduction of tensile contact stresses as a result of the lubricating effect of UHMWPE’s smooth surface and highly entangled chain structure of UHMWPE.

K. Plumlee and C. J. Schwartz (2009) considered number of total joint replacement devices used in orthopedic medicine involving articulation between a metallic alloy and UHMWPE. The authors showed that UHMWPE based composites had good wear resistance comparable to the irradiation crosslinked polymer. However, the selection of the reinforcing material was complicated both by understanding the mechanical behavior of the filler and also by biocompatibility considerations. Zirconium manifested excellent corrosion resistance and biocompatibility, and the authors used the material as reinforcing filler in UHMWPE with promising results. Compression molded UHMWPE composites with up to 20% wt. of micro sized zirconium particles were investigated with regards to wear behavior and impact toughness. The composites showed a significant reduction in wear compared to unfilled polymer while still maintaining impact toughness. These results reinforced the paradigm of using polymer composites for orthopedic applications and might provide a viable alternative to the property tradeoffs encountered with irradiation crosslinking.

In the S. Ge, S. Wang and X. Huang (2009) work, the natural coral (NC) were applied as reinforcement fillers into UHMWPE to increase the wear resistance of UHMWPE composites. The micro hardness and scratch resistance of UHMWPE/NC composites were studied. A hip joint simulator was operated to investigate the wear behavior of UHMWPE/NC composites against CoCrMo balls, the wear tests were lubricated by 25% bovine serum solutions. The wear mass loss and wear debris distribution through one million test cycles were examined in the paper. It was shown that the adding of NC particles in UHMWPE resulted in the enhancement of micro hardness and scratching resistance of the UHMWPE/NC composites. The micro hardness of UHMWPE/NC composites increased with natural coral contents in the linear relationship. The scratch coefficients of UHMWPE/NC composites increased in contents range of 10% wt NC particles, the scratch depth decreased with the increasing NC contents. The wear resistance of UHMWPE/NC composites increased with the increasing contents of natural coral particles. It was found that the relation of wear mass loss of UHMWPE ace tabular cup to the micro-hardness followed a negative power law. The wear mechanism of UHMWPE/NC composites was mainly controlled by adhesive wear. The NC contents in UHMWPE changed the severity of adhesive wear. The investigation of UHMWPE wear debris revealed that adding of NC particles in UHMWPE resulted in variations of size distribution of UHMWPE wear debris.

2.2.2 UHMWPE as toughener in polymer blend and compound

In A.A. Lucas (2011) work, the blends between HDPE and UHMWPE were obtained by mixing in a melted state at concentrations ranging from 10 to 30% by weight in an intermeshing co-rotating twin screw extruder (ICTSE). The abrasive resistance of the blends was evaluated according to the DIN53516 standard, and it was observed that the volumetric loss of the blends decreased with increasing concentration of UHMWPE. The mechanical properties of the samples were analyzed in terms of flexural, tensile, and impact strength; in general, the HDPE/UHMWPE blends had a good set of properties, most of which were better than the properties of pure HDPE. Thermal analysis of samples was made by differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA), and no significant difference was observed between the blends and pure HDPE.

G. Sui et al., (2009) investigated the effects of untreated and pretreated carbon nanofibers(CNFs) on the crystallization behavior, friction behavior, and mechanical properties of UHMWPE/HDPE nanocomposites. Composite was prepared by a twin screw extrusion. The degree of crystallinity, and the tensile strength and modulus of the UHMWPE/HDPE systems exhibited an increasing trend initially with addition of CNFs, followed by a decrease at higher contents. With the increasing of untreated CNF content, the friction coefficient of UHMWPE/HDPE was decreased and displayed less change in the process of friction. The enhancement in tensile strength of nanocomposites containing 0.5% wt treated CNFs was four times higher, 32%, than that of the nanocomposites containing untreated CNFs, 8%, over that of the pure polymer.

R. Hashmi et al., (2001) reported a wear resistant polymer. UHMWPE was melt blended with isotactic polypropylene (PP) in different proportions. Sliding wear tests were conducted by using Cameron Plint pin on disc apparatus. Polymer samples in the form of the pin were tested against EN24 steel disc at different pressures and sliding speeds. The wear volume of PP reduces significantly on the addition of UHMWPE. At 0.28 m/s sliding speed, wear rate of PP was 15 $x10^{-12}$ m^3/m which reduces to 0:28 x $10^{-12}m^3/m$ on addition of 15% wt. of UHMWPE. At 1.09 m/s sliding speed, PP deforms, while 15% wt. of UHMWPE sample did not show significant deformation. Wear loss of 15% wt. of UHMWPE filled PP blend significantly lowered as compared to PP. Reduction in wear loss of UHMWPE filled

PP blend was attributed to the reduction in temperature of contact surface. Worn surface of the test sample showed two distinct morphological regions.

2.3 HDPE Blends and Compounding

M. Palabiyik and S. Bahadur (2002) studied the mechanical and tribological behaviors of PA6 and HDPE blends made using maleic anhydride polypropylene as the compatibilizer. The compositions investigated for tribological behavior were 80% wt. of PA6 to 20% wt. of HDPE and 60% of PA to 40% wt. of HDPE. The polyblends were reinforced with glass fiber (GF) and filled with PTFE and copper oxide (CuO). The friction and wear experiments were run under ambient conditions in a pin on disk machine. The tensile strength of the polyblend increased with increasing fiber content but the material became brittle. With the additions of PTFE in two proportions, the steady state coefficients of friction of 80% wt. PA6 and 20% wt. HDPE decreased significantly while the reductions in case of 60/40 PA6/HDPE were smaller. There was no advantage seen in terms of either the coefficient of friction or wear rate by adding CuO to the polyblends with 10% wt. of PTFE. GF reinforcement neither reduced wear nor the coefficient of friction of the polyblend. Of all the methods used to improve the tribological behavior of the polyblends, 10% PTFE as the filler was the most effective.

M. Palabiyik and S. Bahadur (2000) investigated the effect of compatibilizer HDPE-g-MAH of different contents on the transfer and tribological behaviors of PA46/HDPE blends. The wear of the polyblends was reduced when the compatibilizer ranged from 1 to 5% wt. Scanning electronic microscopy (SEM) and Energy

Dispersive Spectroscopy (EDS) analyses were used to examine the worn surface and the physical state of the acid eroded transfer films on the counter face. It was found that the physical bonding between PA46 and HDPE phases became stronger due to the better compatibility of the polyblends counter face, and ultimately decreased the wear.

F. Xiang et al., (2006) studied the mechanical and tribological properties of PA6 and HDPE blends with and without the compatibilizing agent, maleic anhydride propylene. This study attempted to understand the tribological behavior of PA6 and HDPE polyblends with and without compatibilization in light of the structure and mechanical properties. Proportion was high enough for interaction with PA6 and HDPE interface. The mechanical properties were studied in terms of the tensile strength, hardness and elongation at break. Friction and wear experiments were run under ambient condition in a pin-on-disk machine. It was found that the tensile strength of polyblends increased when polyamide proportion was more than 20% wt. and hardness increased with any polyamide proportions. The best polyblends for low coefficient of friction and high wear resistance were 60/40 and 80/20 of PA6/HDPE blends.

The thermo mechanical recycling of post consumed plastic bottles was studied by A. Vila, et al., (2003) especially the ones made of PET/HDPE blends and its use as composite materials for engineering applications. To be able to evaluate the new composite performance from the mechanics point of view; i.e. stiffness and machine ability, two sets of tests were carried out. For the first set, compression tests were applied. For the machine ability evaluation, the final roughness was measured after the milling procedure at different speeds and leads. Experimental data showed good performance for compression and machine ability. Finally, spur gears were cut from cylindrical specimens made of PET/HDPE blend.

A nanocomposite based on a PP/HDPE blend was presented by F.C. Chiu, H.Z. Yen and C.E. Lee (2010). The polymer composite were prepared using an organomontmorillonite (15A) as a nano filler and two maleated polyolefins, PE-MA and PP-MA, as compatibilizers. The phase morphology and typical physical properties of the prepared samples were examined. The nano filler, 15A, was intercalated and/or partially exfoliated in the blend when PE-MA or PP-MA was present. The PE-MA facilitated the dispersibility of 15A to a better degree. The nano filler, 15A, accelerated the crystallization of PP in the blends, whereas it hardly influenced the crystallization of HDPE. Moreover, at a slow cooling rate, the PP-MA induced a higher crystallization temperature for PP in the composite, while PE-MA impeded PP crystallization. On the other hand, the crystallization of HDPE in the composite was only slightly influenced by the presence of PE-MA or PP-MA. The thermal stability of PP/HDPE blend was enhanced after the addition of 15A regardless of the inclusion or not of PE-MA or PP-MA. The enhancement was more evident when the samples were scanned under an air environment than in N_2 environment. The stiffness of PP/HDPE blend increased marginally after adding 15A and was slightly altered with the further inclusion of PP-MA. The presence of PE-MA in the composite caused a slight decline in the stiffness. The impact strength of PP/HDPE blend declined after the formation of nanocomposites, especially for the sample incorporating PP-MA.

Banana fiber (BaF) reinfored composites based on HDPE/PA6 blend was presented by H. Liu, Q. Wu and Q. Zhang (2009). The polymer composite was prepared via a two steps extrusion method. Maleic anhydride grafted styrene/ethylene–butylene/styrene triblock polymer (SEBS-g-MA) and maleic anhydride grafted polyethylene(PE-g-MA) were used to enhance impact performance and interfacial bonding between BaF and the polymer resins. Mechanical, crystallization, melting, thermal stability, water absorption and morphological properties of the composites were investigated. In the presence of SEBS-g-MA, better strengths and moduli were found for HDPE/PA6 based composites compared with corresponding HDPE based composites. At a fixed weight ratio of PE-g-MA to BaF, an increase of BaF loading up to 48.2% wt. led to a continuous improvement in moduli and flexural strength of final composites, while impact toughness was lowered gradually. Predicted tensile modulus by the Hones Paul model for three dimensional random fiber orientation agreed well with experimental data at the BaF loading of 29.3% wt. However, the randomly oriented fiber models underestimated experimental data at higher fiber levels. It was found that the presence of SEBS-g-MA had a positive influence on reinforcing effect of the Nylon 6 component in the composites.

The processing of the PA12 and HDPE blends by Selective laser sintering using a CO_2 laser was investigated by G.V. Salmoria, et al., (2008). Mixture composition, processing conditions and their influence on the dynamic mechanical properties of the specimens manufactured were evaluated. As expected, the average value for the elastic modulus of PA12 was higher than that for the HDPE specimens. The low values of ultimate strength obtained for the PA12/HDPE at 80/20 and 50/50 specimens indicated the low chemical affinity between the PA12 and the HDPE domains. The microstructures of the PA12/HDPE blend specimens were heterogeneous with co-continuous and disperse phases depending on the quantity of

HDPE. The higher ultimate strength of PA12/HDPE at 20/80 was due to the greater HDPE content in the blend, which provided higher toughness. The creep and fatigue behavior also changed as a function of the component quantities.

In S. Wu, G. Ji and J. Shen (2003) work, the oxygen containing groups such as C–O, C=O and C(=O)O were introduced onto the molecular chain of HDPE by ultraviolet irradiation in air. The content of these groups increased with increasing the irradiation time. After irradiation, the molecular weight and melting temperature of HDPE decreased, and the degree of crystallinity and hydrophilicity increased. Adding a small amount of irradiated HDPE to the HDPE/polyvinyl alcohol (PVA) fiber composites improved their mechanical properties. Compared with that of HDPE/PVA fiber at 85/15 composite, the yield and impact strength of HDPE/PVA fibre, at 75/15, composites made compatible with 10% wt. of HDPE irradiated for 48 h were increased from 32.6 MPa and 480 J/m to 40.5 MPa and 532 J/m, respectively.

2.4 PTFE Composites and Applications

The friction and wear behavior of PTFE filled with potassium titanate whiskers (PTW) were studied by F. Xin, et al., (2006). The purpose of this work was to study the friction and wear properties of the PTFE composites reinforced with various amount of PTW under dry sliding conditions. The crystallization of the composites, the abrasive dust and the worn surface were also investigated. It was shown that the friction coefficient of PTW/PTFE composites decreases with the increase of PTW content. The crystallization of the composite was measured by differential scanning calorimeter (DSC). The relationship between the degree of crystallization and the wear behavior was also analyzed which reveals the effect of

PTW on PTFE. It was also manifested that the increase of crystallization improved the wear property.

F. Xin, et al., (2007) also investigated the mechanical properties, thermal deformation temperature, tribological performance and corrosion resistance of PTW reinforced PTFE composites. They varied the contents and sizes of PTW in PTFE. For the small size PTW at 5% wt., the tensile strength, elongation at break, notched impact strength, thermal deformation temperature and wear resistance were simultaneously increased. When filler size was increased, the tensile strength, elongation and hardness were decreased, while the wear resistance and thermal deformation temperature were improved.

In D.K. Sarkar, M. Farzaneh and R.W. Paynter (2008) work, super hydrophobicity had been demonstrated on ultrathin Teflon coated etched aluminum surfaces. The etching of aluminum surfaces were performed using dilutes hydrochloric acid. An optimized etching time of 2.5 min was found to be essential, before Teflon coating, to obtain a highest water contact angle of 164±3° with a lowest contact angle hysteresis of 2.5±1.5°, with the water drops simply rolling off these surfaces with even the slightest inclination of the sample. The presence of $-CF_3$ radicals along with $-CF_2-$ radicals in the ultrathin Teflon films, as investigated by X-ray photoelectron spectroscopy (XPS), contributes to the lowering of the surface energy on the aluminum surfaces. The presence of patterned microstructure as revealed by field emission scanning electron microscope (FESEM) together with the low surface energy ultrathin Teflon films rendered the aluminum surfaces highly super hydrophobic.

In B. Serra (1999) work, a bi-enzyme electrode was fabricated by simple physical inclusion of the enzymes and the mediator in the bulk of the graphite Teflon matrix. A Teflon content of 70%, and a pH of 7.4 were employed as working conditions. The composite bio-electrode exhibited long term operation because of the renewability of its surface by polishing. Reproducible amperometric responses were achieved with different electrodes fabricated from different composite matrices, and no significant loss of the enzyme activity occurred after 6 months of storage at 4°C. Detection limits for L-lactate of 1.4 and 0.9 µm were obtained by batch amperometry in stirred solutions and flow-injection with amperometric detection, respectively. An interferences study with different substances which might be present in wine and yogurt together with L-lactic acid demonstrated very good selectivity for the determination of this analyst. The bi-enzyme composite electrode was applied to the determination of L-lactic acid in red wine and shaken yogurt, and the methods were validated by comparing these results with those obtained by applying a recommended reference method.

Y. Han et al. (2012) studied how the transformer oil flow rate affected the permeation characteristics of transformer fault gases in the ceramic/Teflon-AF2400 composite membrane. They compared the permeation characteristics of the gases in the dissolved state and the gas state. When the oil flow rate increased from 250 to 750 ml/min, the equilibrium time of H_2 and CO reduced by about 40% while that of C_2-hydrocarbons had little change, which indicated that the gas diffusion in the oil somewhat affected the oil/gas separation. The C_2 hydrocarbons first reached permeation equilibrium in the dissolve state, whereas H_2 first reached permeation equilibrium in the gas state. The FTIR results indicated that after immersion in the transformer oil, the Teflon AF2400 membrane absorbed some transformer oil that formed a structure similar to supported liquid membrane. The solubility of the gases in the oil determined their permeation characteristics during the transformer oil/gas separation.

2.5 PTFE Deposition and Friction Improvement

H. Schonher and G. J. Vancso(1997) published the research work on SEM and scanning force microscopy(SFM) study on the surfaces of the worn PTFE and PE sliders used for friction deposition of PTFE or PE onto glass substrates. These surfaces exhibited a fibrillar morphology which was oriented in the sliding direction. The molecular order of the PTFE and PE chains on the surface of thin microfibrils on the slider could be readily imaged with molecular resolution using SFM. The SEM and SFM images presented direct evidence of an orientation of the slider on both a fibrillar and a molecular level. The orientation occurred during shearing of the material that was stuck onto the glass surface due to the high adhesion between the first layer of PTFE and the glass. The orientation of the worn surface of polymeric sliders could be visualized on different length scales: fibers, fibrils, microfibrils and the polymer crystal structure could be observed. The polymer chain direction on top of the microfibrils was corresponded to the sliding direction.

In C. Gu (2006) report, solid lubricant composite material was made by compression molding PTFE and ultra fine kaolin particulates. Composites from 0 to 15% wt. were prepared. These composites were tested against a 45 carbon steel counterface on a reciprocating tribometer. The experimental conditions were a contact pressure of 7.5 MPa, a stroke length of 15 mm, and a reciprocating frequency of 1 Hz.

The friction coefficient of the composites increased over unfilled PTFE from roughly 0.12 to 0.22, at filler concentrations of 10% wt., the wear resistance improved by almost two orders of magnitude as compared to the unfilled PTFE. Wear testing and SEM analysis showed that adhesive wear was probably the dominant mode of failure for PTFE 10% wt. kaolin composite.

Y. Wu, et al. (2006) revealed the friction behavior and wear mechanism of electroless Ni–P matrix with PTFE and/or SiC particles composite coating by virtue of ring on disk wear machine at a high load of 150 N. The worn surface, wear debris and the composition changes after wear were characterized using scanning electron microscopy (SEM) and energy dispersive analysis of X-ray (EDAX). By comparison with Ni–P and Ni–P–SiC coatings, the results indicated that the combination of a PTFE rich mechanical mixed layer (PRMML) formed on the worn surface and hard SiC were responsible for the good tribological properties of the hybrid Ni–P–PTFE–SiC composites at high load. After heat treatment at 400^{o}C for 1 hour, the wear rate of Ni–P matrix composites decreased with corresponding to the increase in micro hardness. During sliding, an obvious decrease in the temperature rise with PTFE addition was attributed to the good anti friction of PTFE.

A solid lubricant composite material between PTFE and 40 nm alumina particles was studied by W. Sawyer, et al., (2003). Prior to compression molding the constituent powders was blended using a jet milling apparatus. Composites from 0 to 20% wt. of PTFE were prepared. These composites were tested against a polished stainless steel counterface on a reciprocating tribometer. The experimental conditions were a contact pressure of 6.4 MPa, a stroke length of 50 mm, and a sliding speed of 50 mm/s. The friction coefficient of the composite increased over unfilled samples from roughly μ = 0.15 to μ = 0.20. The wear resistance of this composite increased monotonically with increasing filler concentration and no optimum filler fraction was found.

M. Khan, et al. (2009) investigated the friction and wear of none modified and electron beam modified PTFE filled EPDM rubber. The pin on disk tribometer showed different behavior during the sliding contact with hard spherical steel ball. The friction coefficient (μ) and specific wear rate (*k*) of modified PTFE filled EPDM increased with an absorbed dose of PTFE powder while none modified PTFE filled EPDM showed the lowest μ and *k* values. This variation in friction and wear behaviour of PTFE filled EPDM compounds was caused by the influence of radiation induced chemical changes in PTFE powder on the radical initiated peroxide crosslinking. It resulted from the lower crosslinking efficiency and consequently in the deterioration of the bulk properties. The electron modification of PTFE powder reduced the hardness, modulus, and increases the energy dissipation, tan δ, of te compounds. Beside other factors, these variations in bulk properties had shown to have deleterious effects on the friction and wear properties of electron beam modified PTFE filled EPDM.

A compositional grading of PEEK and PTFE was investigated by D. L. Burris and W. G. Sawyer (2007) to create a bulk composite with the functional requirements of component strength, stiffness and wear resistance while providing solid lubrication at the sliding interface. The tribological performances of three functionally graded PEEK components were evaluated on linear reciprocating, rotating pin on disk and thrust washer tribometers. Wear rates comparable to samples of the bulk solid lubricant and comparable or improved frictional performance were achieved by compositionally grading the near surface region of PEEK components.

M.S. Khan, et al. (2009) presented the effects of electron beam modification of PTFE powder on the friction and wear properties of PTFE filled EPDM rubber cured by a radical initiated peroxide system. Friction and wear properties of EPDM vulcanizates were determined with the help of pin on disc tribometer in sliding contact with a steel ball at room temperature without lubrication. PTFE powder was modified in atmospheric conditions with low, 20 kGy, and high, 500 kGy, irradiation doses using electron beam accelerator. The spectroscopic investigations revealed that the increasing concentration of reactive free radicals and functional groups with irradiation did have a drastic influence on crosslinking efficiency due to their interference with peroxide radicals in curing process. As a result, none irradiated and low irradiated PTFE filled EPDM with higher crosslinking densities showed remarkably enhanced friction and wear properties. On the contrary, 500 kGy PTFE filled EPDM having significantly lower crosslinking density resulted in poor friction and wear characteristics. The apparent crosslinking density measured directly from the curing curves was found to be the most dominating parameter influencing friction, wear as well as the physical properties.

The friction and wear properties of surface treated carbon nanofiber (CNF) were investigated by Y. Shi, X. Feng, H. Wang and X. Lu (2008). Scanning electron microscopy was utilized to study the worn surfaces of PTFE composites. Experimental results showed that surface modification decreased the friction coefficient of CNF/PTFE composites slightly, and obviously reduced the wear volume loss of the PTFE composites. Among all HNO_3 treatments, 10 minutes treatment was the best for the improvement of anti wear properties of PTFE composites. Moreover, the best anti wear property of the composite was achieved when CNF was treated with HNO_3 followed by coupling agent treatment, which was about 30% lower than that of untreated CNF filled PTFE under 200N load. SEM studies indicated that surface modification could reduce the abrasive wear of CNF/PTFE composites. And the dispersion of CNF in PTFE composites was also improved after the surface modification, especially for the treatment of HNO_3 followed by coupling agent.

2.6 Crosslinking of Polymers

2.6.1 Radiation crosslink

The UHMWPE/nano hydroxyapatite (n-HA) composite was studied by L. Xiong, D. Xiong and J. Jin (2009). The prepared materials were irradiated by gamma rays in vacuum and molten heat treated in vacuum just after irradiation. The effect of filling n-HA with gamma irradiation on tribological properties of UHMWPE was investigated by using friction and wear experimental machine under deionized water lubrication. Micro morphology of worn surface was observed by metallographic microscope. Contact angle and hardness of the materials were also measured. The results showed that contact angle and hardness were changed by filling n-HA and gamma irradiation. Friction coefficient and wear rate under deionized water lubrication were reduced by filling n-HA. While friction coefficient was increased and wear rate was reduced significantly by gamma irradiation. The worn surface of unfilled material was mainly characterized as adhesive wear and abrasive wear, and that of n-HA filled material was mainly characterized as abrasive wear. After gamma irradiation, the degrees of adhesive and abrasive wear for unfilled material and abrasive wear of n-HA filled material were significantly reduced. Unfilled and filled materials after irradiation were mainly shown as slight fatigue wear. The results indicated that UHMWPE and UHMWPE/n-HA irradiated at the dose of 150 kGy can be used as bearing materials in artificial joints for its excellent wear resistance compared to original UHMWPE.

In L. Costa (2009) work, the medical grade UHMWPE was blended with 1.1, 2.3 and 11 mmol/l of vitamin E and consolidated by compression moulding. Small blocks of reference and of vitamin E blended UHMWPE were then electron beam irradiated at 30, 60 and 90 kGy, both in vacuum and in air. FTIR spectroscopy was used to monitor changes in both the polymer and the additive. Thin sections of irradiated virgin and vitamin E blended UHMWPE were aged in air, at room temperature and in the dark and the kinetics of oxidation followed by FTIR. The reaction between vitamin E and macro alkyl radicals or unlikely with peroxy radicals had been demonstrated and a correlation between the decrease of macro radicals and the stabilization effect of vitamin E had been shown.

2.6.2 Chemical crosslink

In A.B. Leonardi (2011) worked on the designed epoxies for large tensile elongations or large recovered stresses. However, meeting these requirements simultaneously was a difficult task because changes in the crosslink density affect both variables in opposite ways. They showed that a shape memory polymers based on an epoxy network with both chemical and physical crosslinked could be strained up to 75% in four repeated shape memory cycles with tensile stresses close to 3 MPa. Shape fixity and shape recovery values were close to 98% and 96%, respectively, for every one of the cycles, without any significant change between the first and subsequent cycles.

In K. Sirisinha (2010) work, HDPE was melt grafted with vinyl trimethoxy silane using dicumyl peroxide as initiator. Three types of ethylene copolymers were used as silane carriers, and were evaluated for their ability to assist the silane grafting and water crosslinking of HDPE. FTIR revealed that an increase in the amount of silane absorbed in the carriers did not help improve the silane grafting efficiency. However, the gel and rheological results showed that those carriers promoted the rate of crosslinking and increased the density of the crosslink network. Ethylene vinyl acetate showed a stronger effect in this respect than ethylene octene and ethylene butene copolymers. Analysis of the crosslinked materials by heat distortion temperature test and thermogravimetric analysis indicated a marked increase in distortion and decomposition temperatures, as well as thermal activation energy, compared to the neat HDPE. The presence of silane induced crosslinked polymer also resulted in a slight improvement in tensile yield stress and modulus.

The use of silane technology in crosslinking polyethylene wood flour composites was investigated by M. Bengtsson and K. Oksman (2006). Composites were produced in a one step process using a co-rotating twin screw extruder. The composites were stored in a sauna and at room temperature to study the effect of humidity on the degree of crosslinking. Crosslinked composites showed improved toughness and creep properties compared to non crosslinked composites. The flexural modulus, on the other hand, was lower in the crosslinked samples than in the noncrosslinked ones. FTIR was used to study the crosslinking reaction in the samples. X-ray mapping of the silicon signal was also performed to locate the silane in the composites. This study provided a basis for proposing, that part of the silane was grafted onto polyethylene and wood thereby creating a crosslinked network in the matrix with chemical bonded, covalent and hydrogen bonding, to wood. The other part of the silane remained unreacted and blended into the system.

The long term performance and properties of the crosslinked polyethylene (XLPE) under thermal and UV ageing conditions were investigated by M. Celina and G. A. George (1995). In their study, characterize of various silane and peroxide crosslinked low density polyethylene samples and to investigate the fundamental processes occurring during the thermal and UV degradation of these materials were attempted. The technique of solvent extraction used to determine the gel content and solvent swelling of the XLPE was shown to be ideally suited to characterize and to monitor the degradation of the XLPE. The two materials differed in relation to the mechanical properties, melting characteristics and network properties of the XLPE, with silane XLPE being generally less homogeneously crosslinked than peroxide XLPE. Various degradation studies revealed that this fundamental difference may also influenced the mechanism of the degradation. Silane XLPE was shown to be more sensitive to the degradation and may be degraded in a more heterogeneous manner than the peroxide XLPE.

2.6.3 Special crosslink

In M. Shirai (1998) work, polymers bearing imino sulfonate units in the side chain were prepared by the radical copolymerization of corresponded monomers and photo assisted thermal crosslinking of the polymers was studied. Although the polymers became insoluble in common organic solvents upon heating, the temperature (T_{ins}), at which they became insoluble, lowered if they were irradiated before heating. The acid generated from the photolysis of imino sulfonate units catalyzed the thetmolysis of the remaining imino sulfonate units, causing the crosslinking of the polymer. The T_{ins}, values were depended upon the structure of imino sulfonate units and also upon glass transition temperature of the polymers. A mechanism for the photo assisted thermal crosslinking of the polymers was discussed.

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CHAPTER III

DESIGN OF EXPERIMENT: POLYETHYLENE AND POLYTETRAFLUOROETHYLENE BLENDS

3.1 Abstract

Polytetrafluoroethylene (PTFE) is added into High density polyethylene (HDPE) to enhance the mechanical and tribological properties of HDPE. In this paper, a 2^k factorial experiment is performed to ascertain the effect of three factors. The factors include PTFE content, silane content and DCP content and evaluating the output data by using analysis of variance method (ANOVA) to identify the effects of PTFE content, silane content, and DCP content and more importantly their interaction effects on the mechanical behavior of the HDPE/PTFE blends. The macro chain crosslink via the silane/water condensation and during the sauna treatment and also the increasing in the crystallinity of the semicrystalline polyolifins during prolong annealing at temperature close to their glass transition temperature could have the positive effect on the most physical and surface properties of the blends. Form the statistical results obtained, the DCP content (**-C**) and interaction amount between PTFE and silane (**-AB**) used for manufacturing of HDPE/PTFE blend had negatively and significantly affected to the flow ability of the HDPE/PTFE blend. While, DCP content is negatively and significant effect (**-C**) to the flexural strength of the original blend samples. On the other hand, all of assigned parameters and their levels do not

have the significant effect to the flexural strength of the HDPE/PTFE blends underwent sauna treatment. For the flexural modulus of HDPE/PTFE blends, the DCP (-**C**) and silane/PTFE (-**AB**) are the significant variable for the flexural modulus of the original samples. Especially, the DCP (-**C**) is the negative and significant to the flexural modulus of the cured samples as well. The statistically results suggested that DCP, PTFE and silane contents has no significant effect to the Tensile properties, notched impact strength, HDT, surface tension and wear resistance of HDPE/PTFE blends. This preliminary conclusion will be used for further improvement of the properties of HDPE/PTFE blends throughout this study.

3.2 Introduction

Polytetrafluoroethylene (PTFE) or commonly and commercially known as Teflon^{TM} has a very low coefficient of friction at low speeds of rubbing and has the added attraction of being resistant to atmospheric degradation and chemical attack by most substances. However, this polymer shows a high wear rate, high processing temperature and high cost.

High density polyethylene (HDPE) has good flow properties and is widely used in commodity markets. It can be transformed by traditional processes of extrusion, blow molding, injection molding, and rotational mold. HDPE is a polymer commonly used in pipes for water supply, sewage, and the three-layer coating of steel pipes, with the primary function of protecting the pipes from damage caused by corrosion,. HDPE has excellent low temperature flexibility, low cost, resistance to moisture permeation, and good tribological properties. Such as resistance to abrasive wear which becomes an important factor since the coating is always in contact with sand soil, or with solid particles suspended on water or rubbing against solid particles located at the contact between the surface of the pipe, coated or not, and other surfaces during storage, transportation, installation and usage. The properties of HDPE can be further improved by the various polymer technology means. HDPE blending with other polymers is the most common approach to enhance the properties of this olefin polymer. Compounding the polyethylene with filler(s) and additive(s) is also found as one of the most effective and short cut methods to obtain the better polyethylene compound materials.

In this research work, PTFE was added into HDPE in order to enhance the tribological properties of HDPE without scarifying the mechanical properties. Because of PTFE its self has the outstanding lubricating character. It was thus conceivable that the blends of PTFE and HDPE would be prepared with a reasonable mixed of both polymers properties. An optimum blend of HDPE/PTFE blend should show better wear and friction properties. In this early stage of report, 2^k factorial design of experiment (DOE) was performed to ascertain the effect the blending factors. The main and prime parameters in the HDPE/PTFE blending process include the content of PTFE, Silane and DCP. The silane/DCP system was added as coupling/crosslinking agent in the HDPE/PTFE blend. The crosslinked chains would be induced by the condensation reaction between the free radical initiated siloxane grafted chains with the assisting of water molecule during the sauna incubation or sauna curing. Hence, the physical inter lock or perhaps the chemical bonding by the network chains on the PTFE phase would be formed. Consequently, good interfacial interacted blend would be obtained.

Generally, analysis of variance (ANOVA) and regression techniques are useful to determine if there is a statistically significant difference between the treatments, or parameters, and the designed levels of the parameters. After calculating the main effect and interaction effect of factors then graph plotting between standardized normal probability and effect of factor into the normal probability plot. The significant effect from the normal plot was again taken into the evaluation by ANOVA. The statistical mean of the possibly significant effect parameter(s) would be concluded. In this work, the commercial computer software, Design Expert^{TM}, was used to assist all of the necessarily statistical calculations. The level of significant (α) or the degree of confident to accept the test results was assigned at 0.05 or 95% co. Based on *P*-value from statistical calculation if the calculated *P*-value is less than 0.05, it is implied that statistical model and also the given factor(s) were significant. Eventually, the accepted factor(s) derived from ANOVA conclusion was used to construct the prediction regression model(s). The obtained model formula would be benefit to estimate the properties of HDPE/PTFE blend manufactured from the given level of the blend ingredient(s).

3.3 Research methodology

3.3.1 Materials and chemical reagents

High density polyethylene (HDPE, EL-Lene H5814J), is the general purpose high density polyethylene resin that suitable for injection molding process. It was used as the main polymer matrix. This processing graded HDPE has good flow ability and design for high productivity with good toughness product. It is kindly supplied from SCG-Chemical Co., Ltd. The property of the HDPE matrix used in this study that was supplied from the manufacturer is summarized in Table 3.1.

Table 3.1 Properties of HDPE, EL-Lene H5814J

Properties	Test Method	Value, Unit(SI)
Melting Temperature	ASTM D2117	131^{o}C
Melt Flow Index	ASTM D1238@190/2.16	14 g/10min
Notched Izod Impact	ASTM D256	2 kJ/m^2
Tensile Strength at Yield	ASTM D638@50 mm/min	27.5 MPa
Elongation at Break	ASTM D638@50 mm/min	620%
Flexural Modulus	ASTM D790	1225 MPa
Heat Deflection Temperature	ASTM D648@0.455 MPa	75^{o}C

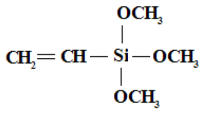
PTFE, Zonyl® MP 1300 fluoroadditive, is a free flowing white powder designed for using as an additive in other materials to impart low surface energy and other fluoro polymer attributions. It is available from DuPont® and it was employed as dispersed phase. According to the manufacturer data sheet, the powder has the particle size of 12 μm. Other properties of the powder provided by the supplier are summarized in Table 3.2.

Table 3.2 Properties of Poly(tetrafluoroethylene), Zonyl® MP 1300

Properties	**Test Method**	**Value, Unit**
Melting Temperature	ASTM D4894	325 ± 5^{0}C
Particle Size Distribution	Laser Microtrac	12 µm
Specific Surface Area	Nitrogen Adsorption	1.5 - 3.0 m^2/g
Average Bulk Density	ASTM D4894	0.425 kg/l

Low viscosity and water clear liquid vinyltrimethoxy silane (VTMS), commercialized as Silquest® A 171, was used as crosslink system in conjunction with peroxide through the moisture incubation or sauna treatment. The chemical structure and physical properties of the liquid silane is given in Table 3.3. The chemical was directly used without further dilution and purification.

Table 3.3 Properties of VTMS, Silquest® A171

Properties	**Value, Unit**
Chemical structure	 $CH_2{=}CH-\overset{OCH_3}{\underset{OCH_3}{Si}}-OCH_3$
Boiling point	122^{o}C
Specific gravity, 25°C	0.967 g/ml

Low melting temperature, $<50^{o}$C, solid dicumyl peroxide (DCP) flake was employed as free radical generator. It is a commercial grad and available throughout the rubber chemicals suppliers. The chemical formula of this peroxide is shown in figure 3.1. Again, it was used without further purification. It has low melting point, slightly above 50°C. It is normally decomposed and generated quit stable free radical at the temperature above 120°C.

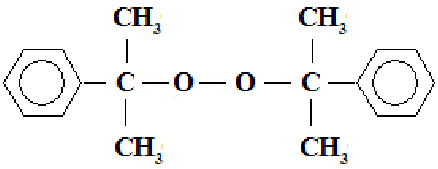


Figure 3.1 Chemical structure of dicumyl peroxide ($C_{18}H_{22}O_2$)

3.3.2 Design of Experiment

Factorial designs were originally developed in the context of agricultural experiments and are now used in other areas including engineering and marketing research. Their use in the medical and behavioral fields has been limited. However, there have been a number of papers discussing the usefulness of these statistical designs in medication and intervention trials. Two levels factorial design is very widely used in research and preliminary analysis. It can reduce time for experiment analysis because they can analysis many factors in the same time and can weed out unimportant or insignificant factor(s) of the experiment. Each of parameter has two levels, assigned as low and high levels. In each level, it could also further divided into two sub levels. Table 3.4 is shown the parameters and their levels that were used for designing the experiment in this research study. To determine, or at least estimate, the factor effects, which indicate how each of factor(s) had the affects to the process output and could be used to adjust the optimized process output. The designed matrix resolved form the given parameters (k = 3) interested in this work was demonstrated in Table 3.5. The factors include PTFE (A), silane (B) and DCP (C) contents. Therefore eight experimental blending formula or eight statistical runs were constructed. Each of formula is absolutely different from the others in term of the composition of the parameters used. The evaluating of the output data, or statistically responds, obtained from each of the blends was analyzed by the statistical method. The analysis of variance (ANOVA) method to conclude or exclude the effects of the designed parameters; PTFE, silane, and DCP contents, and also their interaction effects on the assigned responds of the blends will be discussed and accomplished.

Table 3.4 The parameter and level of DOE

Parameters	**High(+1)**	**Low(-1)**
PTFE content(A)	20, 15	10, 5
Silane content(B)	2.0, 1.5	1.0, 0.5
DCP content(C)	1.0, 0.5	0.3, 0.1

Table 3.5 Design matrix of both actual and coded factor levels

Run No.	**HDPE(g)**	**PTFE content** (g)(**phr**)	**Silane content** (g)(**phr**)	**DCP content** (g)(**phr**)
1	400	(+)80(**20**)	(+)8(**2**)	(+)4(**1**)
2	400	(+)60(**15**)	(+)6(**1.5**)	(-)1.2(**0.3**)
3	400	(+)80(**20**)	(-)4(**1**)	(+)2(**0.5**)
4	400	(+)60(**15**)	(-)2(**0.5**)	(-)0.4(**0.1**)
5	400	(-)40(**10**)	(+)6(**1.5**)	(+)2(**0.5**)
6	400	(-)20(**5**)	(+)8(**2**)	(-)0.4(**0.1**)
7	400	(-)40(**10**)	(-)2(**0.5**)	(+)4(**1**)
8	400	(-)20(**5**)	(-)4(**1**)	(-)1.2(**0.3**)

3.3.3 Melt mixing of HDPE /PTFE blends

The melt mixing procedures between HDPE and PTFE conducted in this research work is schematically summarized in Figure 3.2. The PTFE was pretreated with silane/DCP as batch wise process in the internal mixer. The calculated amount, with respected to 100 g of PTFE powder, of 0.5 phr of DCP was dissolved in 1 phr of silane. The clear solution was promptly added into the PTFE powder in the mixing chamber equipped with the roller rotors. The dry blending was performed at 100^{o}C and rotors speed of 80 rpm for 5 minutes. The treated powder was emptied and stored in tightly closed container at least overnight.

HDPE was pre dried in the vacuum oven at 80^{o}C for 2 hours. The solution of the desired amount of DCP and silane as given in Table 3.5 was dissolved. It was vigorously mixed with the dried HDPE pellet. Then, the pre calculate amount of treated PTFE were added into the HDPE ingredient and completely well mixed. The solid mixture was immediately fed via the single screw feeder into intermeshing co-rotating twin screw extruder having the screw diameter of 25 mm, L/D ratio of 20 and consisted of three quadrate kneader disk. The compounding processing was carried out at screw speed of 10 rpm at the constantly barrel temperature of 190^{o}C for all 4 zones. The compounded strand was cut into rectangular pellet.

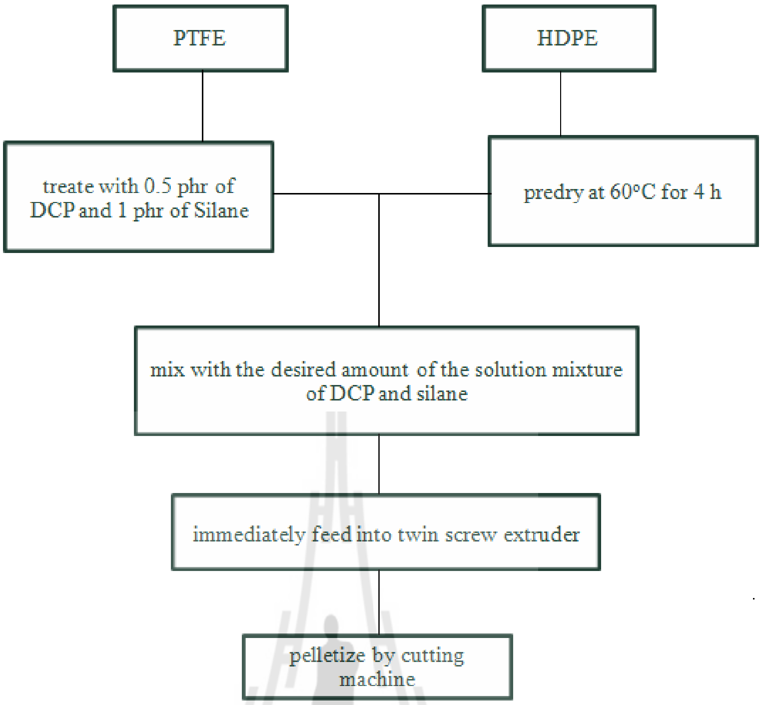


Figure 3.2 Sample preparation charts of HDPE/PTFE blends

3.3.4 Specimen Preparation

3.3.4.1 Specimen for mechanical testing

The tensile, flexural and impact testing samples were prepared by injection molding using a reciprocating screw injection molding machine, CHUAN LIH FA T80. The temperatures profile for molding was 190, 200, 210 and 220^{o}C from feed to nozzle, respectively. The family and artificially balanced two plate mold consisted of two dumb bells, type 1 and type 4, one rectangular bars for flexural and HDT testing and one short rectangular bar for impact testing was employed. The size and shape of the injected specimens were in accordance with ASTM regulations. The temperature of mold cooling water was carefully controlled at 30^{o}C. The injection pressure was electronically controlled at 80% of the maximum machine capacity. The injected samples were divided into 2 sets. The first one was allowed to anneal at room temperature overnight and they was categorized as “**original**” sample. The later was undergone post curing in the sauna oven saturated with moisture at 65^{o}C for at least 12 hours. The incubation temperature was far above the T_g of HDPE. These specimens were classified as sauna cured or shortly as “**cured**” sample.

3.3.4.2 Sheet film preparation

Thick film samples for the abrasion testing were obtained by hot compression press. The compound pellet was placed in between two PTFE/Glass woven sheets. The sample was transferred into the plat molds. The mold was preheated at 200^{o}C for 10 min then slowly pressed at 110 MPa at 200^{o}C for 6 min. The pressed film was immediately removed and allowed to cool down at room temperature. The smooth film with the approximate thickness of 0.4 mm was obtained. The abrasion test specimen was scissor cut into the disk shaped with the diameter of 4.5 cm. The centered hole was punched. The sheet sample was also divided into 2 types, original and sauna cured, respectively.

3.4 Properties Measurement

3.4.1 Rheological testing

The rheological property by mean of melt flow index (MFI) was conducted. The MFI of the HDPE/PTFE pellet was tested in accordance with ASTM D 1238 using the Kayeness melt flow indexer model 4004. The obtained pellet samples from vacuum dried in the oven at 80°C for at least 2 hours to eliminate the possible moisture residual. Testing samples was allowed to completely molten at

230^{o}C for 240 seconds and it was driven through the capillary die (Ø 1 mm.) using piston load of 5.0 kg. Three cuts were performed at the cut times of 30 second. The extrudate was weighed and calculated into the melt flow index in the standard unit of g/10min.

3.4.2 Physical properties

3.4.2.1 Impact strengths testing

Impact strengths of the HDPE/PTFE blends were tested in according with ASTM D 256 in the Izod mode. The injection molded specimen obtained with the dimension of 12x50x3 mm. was notched using the notching machine. The identical injected samples were tested without notching. Notched and unnotched impact strengths were conducted at room temperature using the impact pendulum with impact energy of 2.7 Joule for the notched specimen and 5.4 Joule for the unnotched sample, respectively. The impact values were reported as impact strength, kJ/m^2, that were calculated from impact energy required for completely breaking the sample over the cross section area at fractured area. At least five samples were tested for each polymer sample and the average value were obtained and recorded.

3.4.2.2 Flexural testing

Flexural properties by mean of the strength and modulus of the HDPE/PTFE sample were examined in accordance with ASTM D790. The injection molded sample with the dimension of 12x120x3.5 was used for the test. Instron universal testing machine, model 5565, with the load cell of 5 KN and three point bending test fixture with span length of 56 mm, 16 times of the thickness, was employed. The crosshead speed of 50 mm/min was constantly controlled. The test specimen was placed plat wise to the bending load. The test was conducted at room temperature in normal atmospheric condition. The flexural strength and modulus were computerized using the following equation (3.1) and (3.2), respectively.

$$\textbf{Flexural Strength} = \frac{3PL}{2[bd]^2} \quad \text{……..(3.1)}$$

Where: P = load at a given point on the load-deflection curve (N)
L = support span (mm)
b = width of beam tested (mm)
d = depth of beam tested (mm)

and

$$\textbf{Flexural Modulus} = \frac{L^3 m}{4(bd)^3} \quad \text{……..(3.2)}$$

Where: L = support span (mm)
b = width of beam tested (mm)
d = depth of beam tested (mm)
m = slope of the tangent to the initial straight line portion of the load-deflection curve (N/mm) of deflection.

3.4.2.3 Heat deflection temperature testing

Heat deflection temperature (HDT) of the HDPE/PTFE blend was conducted with the ASTM D 648. The sample was tested in the edgewise position, with the support span length of 100 mm. The simple beam with the standard load applied at its center to give maximum stress of 0.455 MPa or 66 psi was followed. The testing machine from Atlas, model HDV 1, was employed. The raising temperature at a uniform rate of 2±0.2^{o}C/min was assigned. Liquid silicone oil was used as heating transfer media. The HDT value was reported in degree Celsius (^{o}C) as soon as the specimen had been deflected to 0.25 mm or 0.01 inch that monitored by the dial gauge. This temperature was recorded as the deflection temperature under the assigned standard flexural load of the test specimen. Three samples were examined and the average value was reported.

3.4.2.4 Tensile measurement

Tensile properties of HDPE/PTFE blends were examined using an Instron universal testing machine, model 5565, with a load cell of 5 kN, crosshead speed of 50 mm/min and a gauge length of 80 mm. Tensile tests were performed according to ASTM D638. The dimension of the molded dumbbell shaped specimens with 12.7 mm in width at narrow section, 20 mm in overall width, 80 mm in gauge length, 165 mm in overall length and approx. 3.5 mm in thickness was used for performing the test. Five samples were tested in each blend sample. Calculated tensile strength (N/m^2 or Pa) was given by dividing the maximum load, in Newton force (N), by the average original cross sectional area in the gage length segment of the specimen in square meters (m^2). Calculated modulus of elasticity was performed by extending the initial linear portion of the load extension curve and dividing the difference in stress corresponding to any segment of section on this straight line by the corresponding difference in strain. Calculated percent elongation at break was computed by reading the extension at the fracture point and then dividing that extension by the original gage length and multiplies by 100.

3.4.3 Surface properties observation

3.4.3.1 Wear testing

Wear ability of the blend by mean of abrasion testing was investigated. The standard method namely ASTM D 4060, Abrasive Wear Testing, was followed. It is the measurement of the weight loss under the specified test conditions. In this study, specimens were abraded at 500 rounds of rotation under the constant load at 0.25 kg. The weight loss of the sample was recorded as the below calculation. Three circular HDPE/PTFE blend sheet prepared by the procedure describe in section 3.3.4.2 was employed. Each of specimens was tested. The averaged the weight loss was presented.

$$\textbf{\%Weight loss} = \left[\frac{\text{Weight before test} - \text{Weight after test}}{\text{Weight Before test}}\right] \times 100 \qquad \text{……..(3.3)}$$

3.4.3.2 Water drop diameter observation

The surface tension of the polymer film is normally tested by surface angle measurement using the appropriate test liquid. At the presence time, such expensive equipment is not available in the research laboratory. Attempting to investigate the surface tension of HDPE/PTFE film was conducted by using the adaptive, or comparative, test method. The deionized water was used as the test liquid. The adopted method to evaluate the surface tension between the test liquid and the surface of the injected blends specimen or film were constructed. The micro pipette with the minimal volume capacity of 20 μl equipped with the micro tip adapter was used for applying the water drop. Drops of 1.0 μl of the deionized water through the micropipette were carefully placed onto the cloth dried surface of the blend sample. The diameter of the water drop (D_{sample}) was measured through the optical micro scope and analyzed digitally. The diameter of the water drop on the commercial PTFE/Glass woven sheet (D_{PTFE}) was obtained and used as referee values. It was assumed that it was the pure surface of PTFE film. Then, the ratio between the diameters of drop on the sample divided by the diameter of drop on the standard PTFE sheet was computed according to the equation 3.4. If the computed ratio is higher than 1.0, it means that the diameter of demonized water on the blend sample is larger than on the PTFE sheet. It indicates that the surface tension of the blend sample is higher than the surface tension of PTFE. Vice versa, if the ratio less than 1.0 is obtained, it reviews that the surface tension of the blend would be lower than the referee PTFE sheet.

$$D_{\text{Sample}}/D_{\text{PTFE}} = \frac{\text{Diameter of drop on sample}}{\text{Diameter of drop on the standard PTFE sheet}} \tag{3.4}$$

3.4.4 Morphological investigation

Morphology of the fractured surface of HDPE/PTFE obtained from the notched impact testing was examined using scanning electron microscope (SEM). The broken piece of specimen was cut in to small piece to fit the SEM sample holder. It was securely attached onto the sample holder. The samples were coated with layers of gold for 8 minutes by ionization before analysis. SEM photograph was taken using JOEL machine model JSM6400 at the typical accelerating voltage of 10 keV.

3.4.5 Interpretation of DOE Analysis Using Design Expert™

The design of experimental (DOE) by mean statistical approach conducted in this research was 2^k factorial method as widely used in experiments involving several factors where it is necessary to study the joint effect of the factors on a response. The *k* components were the interested design parameters. Each parameter (*k*) for each test was divided into two levels. These levels may be quantitative, such as two values of pressure, temperature or time or they might be qualitative, such as two machines, two operators and arbitrarily called “low” and “high”. A complete replicate of such a design requires 2 x 2 x …x 2 = 2^k observations and was called a 2^k factorial design. Suppose that three main factors, A, B, and C at two levels are of interest. The design was called a 2^3 factorial design, and the eight treatment combinations, or designed experimental runs, can now be displayed geometrically as a cube, as shown in Figure 3.3 and using the “+ and –” notation to represent the low and high levels of the factors. Sometime it would be shown as table of matrix.

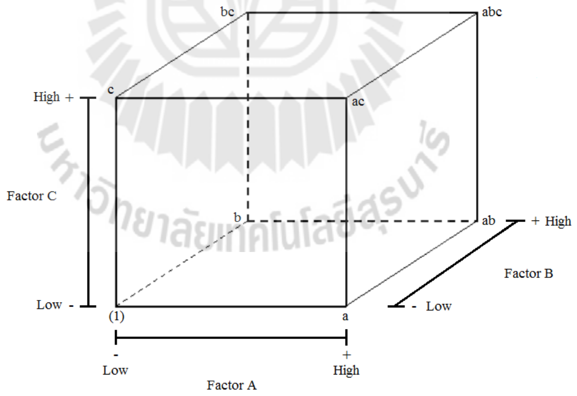


Figure 3.3 Geometric view of 2^3 factorial designs

In first segment of this research, mostly 3 parameter factors that was “2^3” factorial was designed. Then, the total of eight difference treatment conditions or runs of experiments was constructed to evaluating the statistical effects of blends composition factor. One or several responds are needed for analysis. This is called the design matrix as in Table 3.6. There are seven degrees of freedom between the eight treatment combinations in the design. Three degrees of freedom are associated with the main effect and the other associated with interacted effect such as AB, AC, and BC and ABC, respectively.

Table 3.6 The matrix for calculating effects in the 2^3 design

Run	Factorial effect							Effect responds
	A	B	C	AB	AC	BC	ABC	
1	+	+	+	+	+	+	+	
2	+	+	-	+	-	-	-	
3	+	-	+	-	+	-	-	
4	+	-	-	-	-	+	+	
5	-	+	+	-	-	+	-	
6	-	+	-	-	+	-	+	
7	-	-	+	+	-	-	+	
8	-	-	-	+	+	+	-	

The general approach to statistical analysis of 2^k factorial design is summarized into six procedures; *(i)* estimate factor effects (y), *(ii)* form initial model, *(iii)* perform statistical testing, *(iv)* refine model, *(v)* analyze residuals and *(vi)* interpret results.

An alternative to the normal probability plot of factor effects is the half-normal plot. This is a plot of the absolute value of the effect estimates against their cumulative normal probabilities. The straight line on half normal plot always passes through the origin and should also pass close to fiftieth percentile data value.

The degree of significant (α) at 95% confidential was chosen in this study. The calculation of significant level of the experimental data was verified by using Design Expert^{TM} version 7.0.0, which is the commercial statistical software analysis to assist the statistical figures calculation. The significant effects from half-normal plot can be also confirmed by ANOVA testing using the computer program. If *p*-value of the test less than 0.05 indicates that the calculated effect(s) is/are significantly affected by the designed parameter(s).

The effects of factors were calculated by averaging the responses of each factor at the high level (+) and subtracting the average at the low level (-) for same factor as show in equation 3.5.Then, the calculated effects were ranked, *i*, from minimum to maximum.The *p*-value is the area under the normal distribution. According to the design of experiment method, *p*-value is calculated from equation 3.6 where *i* is the rank of effect *I* ($E_{f,i}$). Accordingly, Z-value as cumulative probability, as shown in Figure 3.4 and Table 3.7, are obtained from the conversion of *p*-value using the usual statistic table.

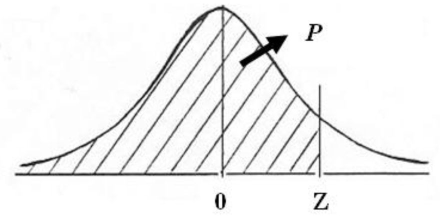


Figure 3.4 Normal distribution curve

$$\mathrm{E}_{f,i} \quad = \quad \bar{\mathrm{F}}_{i(+)} - \bar{\mathrm{F}}_{i(-)} \qquad \text{……..(3.5)}$$

$$p \quad = \frac{i-0.5}{2^{k}-1} \qquad (3.6)$$

Where $\mathrm{E}_{f,i}$ = The effect value of respond *i*

$\bar{\mathrm{F}}_{i(+)}$ = Average response at high level setting of a factor $\frac{\sum \mathrm{Y}(+\mathrm{E}_{f,i})}{\mathrm{n}/2}$

$\bar{\mathrm{F}}_{i(-)}$ = Average response at low level setting of a factor $\frac{\sum \mathrm{Y}(-\mathrm{E}_{f,i})}{\mathrm{n}/2}$

p = Probability

k = Number of factor are used design

i = Rank number of the effect, that order by followed effect value (E_f)

The computer software calculation, the most effect value(s) at the right side in a half-normal plot should be selected before analysis. Keep selecting from right to left until the straight line is matched with the majority of the effects near zero. Notice that the Design Expert adjusts the line to exclude the chosen effect(s). At the point where the process should be end, this line jumps up, leaving a noticeable gap. The effect factors and/or their interactions that lie along the line are negligible and the rest of the effects are significant effects. The trivial effects that have no influence, fall on the straight line near zero effect level, are used to estimate the experimental error.

Table 3.7 Statistical value of factors

Rank (*i*)	Effect value ($E_{f,i}$)	*p*-value	Z-value
1	$E_{f,1}$	$\frac{1-0.5}{2^k-1}$	
2	$E_{f,2}$	$\frac{2-0.5}{2^k-1}$	
3	$E_{f,3}$	$\frac{3-0.5}{2^k-1}$	
...	...	...	
...	...	...	
...	...	...	
2^k-1	$E_{f,2^k-1}$	$\frac{(2^k-1)-0.5}{2^k-1}$	

Pareto chart may help to visualize the magnitude of the chosen effects by displaying them on an ordered bar chart. The vertical axis shows the *t*-value of the absolute effects. This is dimensionless statistic scales in terms of standard deviations. In this case, it makes no difference to the appearance of the half-normal plot. The effects that fall below the bottom limit are non-significant effects. For the effects that fall above the limit are significant effects.

The significant effects from half-normal plot can be also confirmed in ANOVA results. By check the probability or “*p*-value” for the effects which were selected. If the *p*-value less than 0.05 based on the statistical analysis by the ANOVA, it indicates that the effects are significant effects. As the result, the effect of the assigned parameters on the desired respond can be concluded

3.5 Results and discussion

3.5.1 Analysis of MFI

Rheological properties by mean of melt flow index, obtained at 230/5.00, of HDPE/PTFE blend are summarized in Table 3.8. The MFI results were calculated into the standardized effects of the individual parameter and also the interacted parameters by assisting of Design Expert^{TM}. Consequently, the plot of the normal % probability against the obtained standardized effect values, called the normal plot was constructed as given in Figure 3.5. The pareto chart, the plot of the calculated t-values and their ranked, is also presented for the analysis. It is shown in Figure 3.6. According to the normal plot, it is seen that the DCP content (**-C**) and interaction between PTFE and silane content (**-AB**) are negatively effects. They are obviously lined outside the linear trend line. They are suspected as the significant parameter(s) that is effect to the melt index of HDPE/PTFE blend. Considering the pareto chart, both indicators show the t-values above the critical t-value. It reinforces that these two parameters, **-C** and **-AB**, are most likely to be the significant influence on the MFI of the blend. To confirm this postulation, the ANOVA testing was taken into account. The conclusion from ANOVA testing is given in Table 3.9. It is seen that the calculated *p*-values of the designed model and also the parameters **-C** and **-AB** are 0.0036, 0.0024 and 0.0228, respectively, which are lower than the assigned critical value at 0.05 or 95% of statistical testing confidential. It is implied that the designed experiment both parameters and the levels of the parameters; or materials contents, has the significant effect to the flow ability of the HDPE/PTFE blend. The conclusion also reveals that the DCP content (**-C**) and interaction amount between PTFE and silane (**-AB**) used for manufacturing of HDPE/PTFE blend had negatively and significantly affected to the flow ability of the HDPE/PTFE blend. The statistical interpretation from this conclusion means that blending HDPE with PTFE with high content of DCP (**C**) would result in the blend having low melt flow index, high melt viscosity. Also, melt blending with high PTFE loading (+**A**) but low level of silane (-**B**) would give rise to the blended material having low MFI value, high viscosity, and vice versa. The statistical verdict is in good agreement with the science concept. Higher DCP concentration in melt blending of HDPE/PTFE ingredient the more free radical generated. The decomposed active species would react with HDPE chain and vinyl group of VTMS silane to form the reactive sites for further crosslink reaction via the silane/moisture condensation reaction. Hence, the resulted macro crosslinked chains or branched chains would inhibit the flow ability of the molten blend. Therefore, the MFI of the molten blend would be decreased with increasing the DCP concentration in the blend ingredient. The PTFE powder added into the blend would act as polymer filler. The given melt temperature performed in this work, 190^{o}C, and also the viscous heat generated during the melting would not be sufficient to fuse the highly crystalline PTFE powder. Therefore, the solid powder would be only dispersed and mechanical inter locked by the crosslinked HDPE chains. Normally, the viscosity of polymer compound is directly proportional to the filler concentration. Therefore, the higher in PTFE concentration in the HDPE/PTFE shows the lower in the MFI of the blend.

Table 3.8 MFI of HDPE/PTFE blends

Run	HDPE(g)	**PTFE**	**Silane**	**DCP**	**MFI@200/5.00**
		(g) (**phr**)	(g) (**phr**)	(g) (**phr**)	(g/10min)
1	400	(+)80(**20**)	(+)8(**2**)	(+)4(**1**)	0.42±0.22
2	400	(+)60(**15**)	(+)6(**1.5**)	(-)1.2(**0.3**)	5.20±0.64
3	400	(+)80(**20**)	(-)4(**1**)	(+)2(**0.5**)	0.95±0.25
4	400	(+)60(**15**)	(-)2(**0.5**)	(-)0.4(**0.1**)	9.77±0.01
5	400	(-)40(**10**)	(+)6(**1.5**)	(+)2(**0.5**)	3.16±0.55
6	400	(-)20(**5**)	(+)8(**2**)	(-)0.4(**0.1**)	11.54±0.90
7	400	(-)40(**10**)	(-)2(**0.5**)	(+)4(**1**)	0.44±0.06
8	400	(-)20(**5**)	(-)4(**1**)	(-)1.2(**0.3**)	4.42±0.21

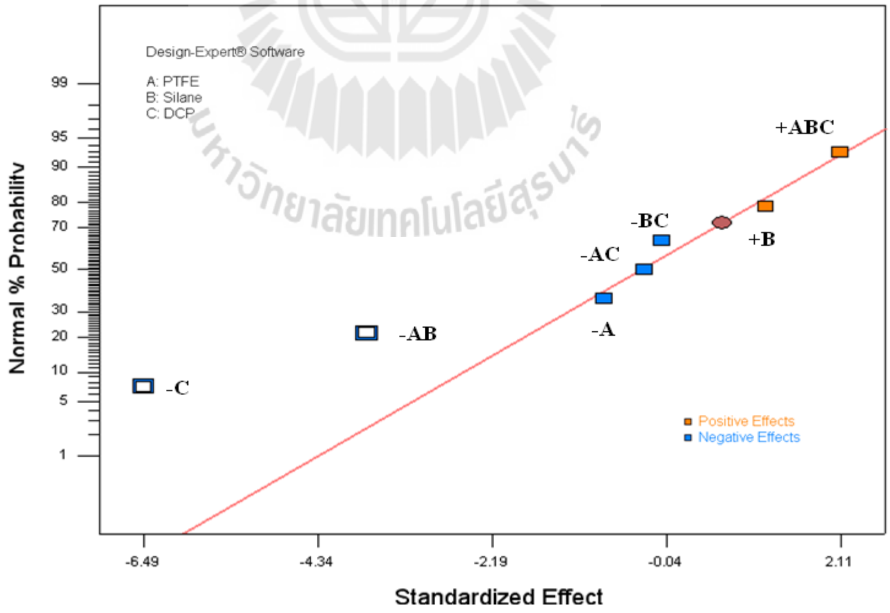


Figure 3.5 Normal probability plot of MFI of the HDPE/PTFE blends

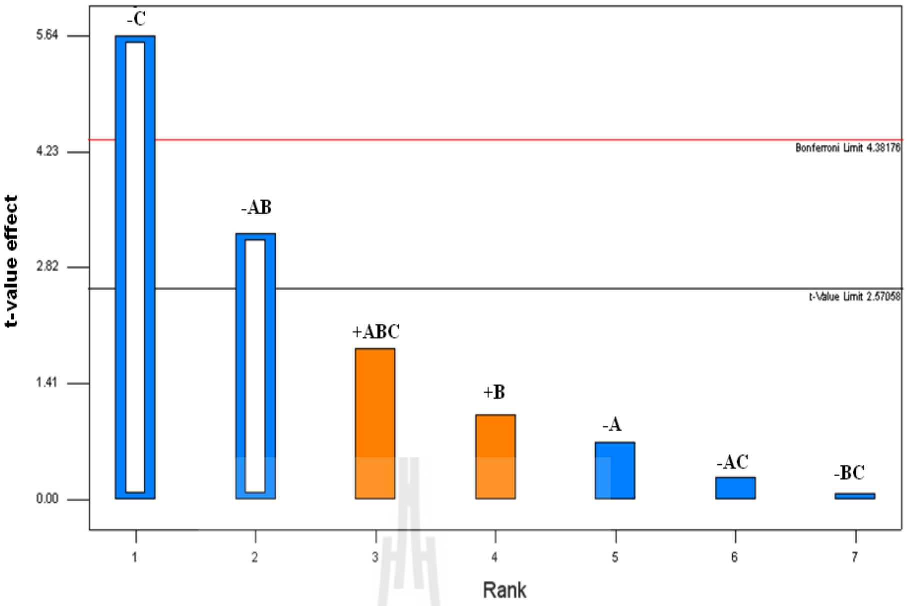


Figure 3.6 Pareto chart analysis of MFI of the HDPE/PTFE blends

Table 3.9 ANOVA test for MFI of the HDPE/PTFE blends

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	112.069	2	56.035	21.195	0.0036
C-DCP	84.209	1	84.209	31.851	0.0024
AB	27.860	1	27.860	10.538	0.0228
Residual	13.219	5	2.644		
Cor Total	125.288	7			

3.5.2 Analysis of flexural properties

Flexural properties by mean of strength and modulus of HDPE/PTFE blend are summarized in Table 3.10 for the original and sauna cured samples, respectively. General observation, the strength value of the sauna cured sample is slightly higher than the original sample. Similarly, the sauna curing increases the flexural modulus of the blend sample except for the blend using low level of silane and DCP (-B and –C), Run#4 where the modulus decrease after sauna incubation. The superior in both strength and modulus through the sauna treatment might be due to the increasing the chain networking formation via the silane/water condensation reaction.

Table 3.10 Flexural properties of HDPE/PTFE blends

Run	**Flexural strength(MPa)**		**Fluxuralmodulus(GPa)**	
	Original	Cured	Original	Cured
1 (+,+,+)	32.91±0.81	34.90±0.83	1.512±0.061	1.608±0.058
2 (+,+,-)	33.16±0.77	36.20±0.66	1.598±0.050	1.774±0.053
3 (+,-,+)	32.85±0.63	34.16±0.46	1.586±0.035	1.626±0.039
4 (+,-,-)	32.94±0.46	34.54±0.57	1.680±0.038	1.670±0.094
5 (-,+,+)	32.95±0.31	35.10±0.46	1.574±0.038	1.688±0.033
6 (-,+,-)	33.92±0.95	36.87±0.88	1.698±0.043	1.812±0.032
7 (-,-,+)	31.77±0.92	34.83±0.86	1.486±0.091	1.654±0.23
8 (-,-,-)	33.92±0.47	36.62±0.96	1.608±0.055	1.790±0.056

Applying the statistical analysis to the flexural strength respond to evaluate the effect of the designed parameters on original sample of the HDPE/PTFE blends using the normal plot, the plot result is given in Figure 3.7. The plot shows that relation between normal % probability and standardized effect of the flexural strength values are formed a linear trend line except for the DCP (**-C**) and interaction between PTFE and DCP (**+AC**) content are excluded from the linear trend line. These two parameters are negative (-) and positive (+) effects to the strength, respectively. They are suspected as the significant effect to the flexural strength of the original sample. The statistical observation is also confirmed again by the pareto chart given in Figure 3.8. It is seen that t-value of DCP parameter (C) is higher than critical t-value but not for the **AC**. It postulates that the DCP content is most likely possible for being the significant effect to the flexural strength of HDPE/PTFE blend before moisture incubation. Finally, the ANOVA testing conclusion given in Table 3.11 is resulted that the calculated *p*-values for the designed model, parameter C and AC are 0.0281, 0.0271 and 0.0556, respectively. It can conclude that the given design parameters for this experiment and the DCP content are significantly effect on the flexural strength of the original blend samples because the obtained *p*-values are less than the given critical value at 0.05. On the other hand, the interacted effect between **A** and **C** does not have the significant effect to the strength of the blends. From the statistical conclusion, it means that, within this research constrain, only DCP content are negatively and significant effect (-**C**) on the flexural strength of the original blend samples. Blending between HDPE and PTFE at low level, less than 0.3 phr, of DCP would provide higher flexural strength of the blend sample before undergo sauna curing than the sample obtained using DCP more than 0.5 phr.

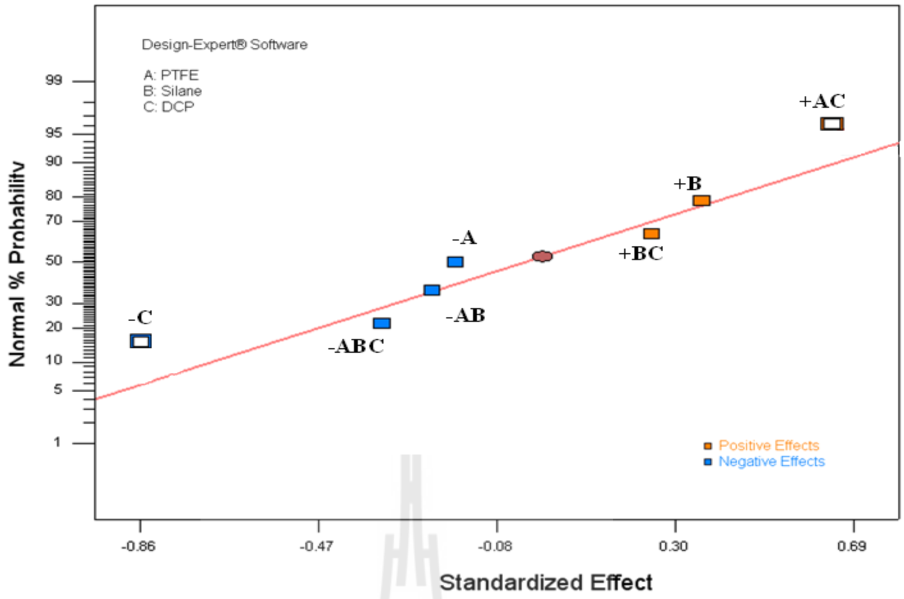


Figure 3.7 Normal probability plot of flexural strength of the HDPE/PTFE blends without sauna treatment

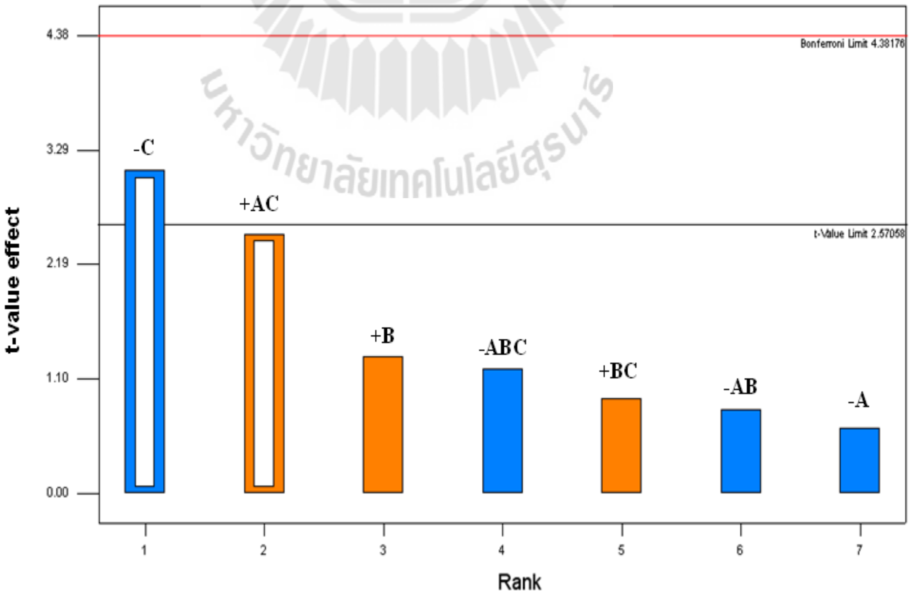


Figure 3.8 Pareto chart analysis of flexural strength of the HDPE/PTFE blends without sauna treatment

Table 3.11 ANOVA test for flexural strength of the HDPE/PTFE blends without sauna treatment

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	2.463	2	1.231	7.858	0.0286
C-DCP	1.496	1	1.496	9.550	0.0271
AC	0.966	1	0.966	6.165	0.0556
Residual	0.783	5	0.157		
Cor Total	3.246	7			

In case of the HDPE/PTFE blend samples undergo sauna curing, the analysis of the flexural by the normal probability plot is shown in Figure 3.9. It is observed that all of the calculated effect values are well fitted with the linear line except for interaction between PTFE and silane content (**+AB**) which is slightly excluded from the group. It means that this positive effect parameter is in doubt to be the significant effect to the flexural strength of the cured blends. Taken the pareto chart, presented in Figure 3.10, in consideration, it is seen that the calculated t-values of all parameters are lower than the critical t-value. Therefore, it assures that the AB+ has no significant effect to flexural strength of the sauna cured sample. The statement is confirmed by the ANOVA conclusion shown Table 3.12. Form ANOVA analysis at 95% of confidential, it concludes that the designed experiment and the suspected parameter do not have the significant effect on the flexural strength because their calculated *p*-values are 0.5551 which are higher than 0.05. Come to this point of discussion, it is firmly to conclude that the levels of the assigned parameters and also the interacted effect between PTFE and silane contents (**+AB**) do not have the significant effect to the flexural strength of the HDPE/PTFE blends underwent sauna treatment.

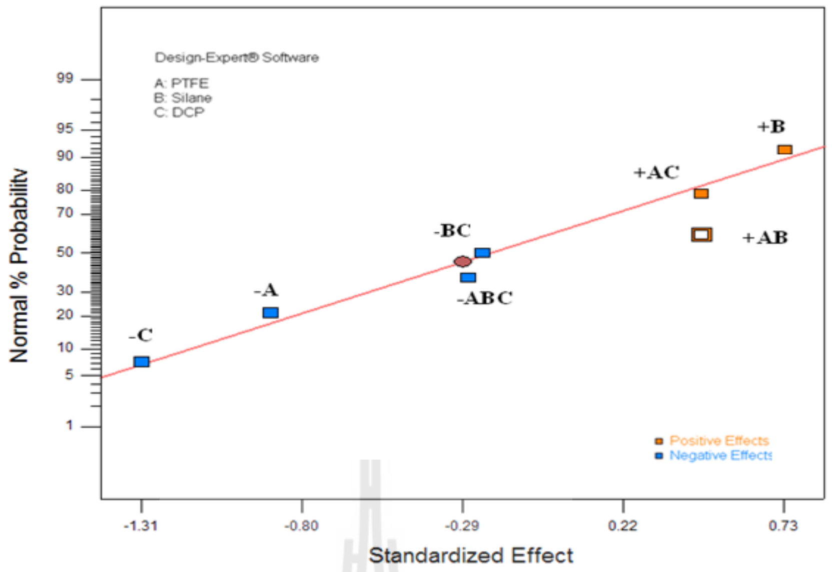


Figure 3.9 Normal probability plot of flexural strength of the HDPE/PTFE blends with sauna treatment

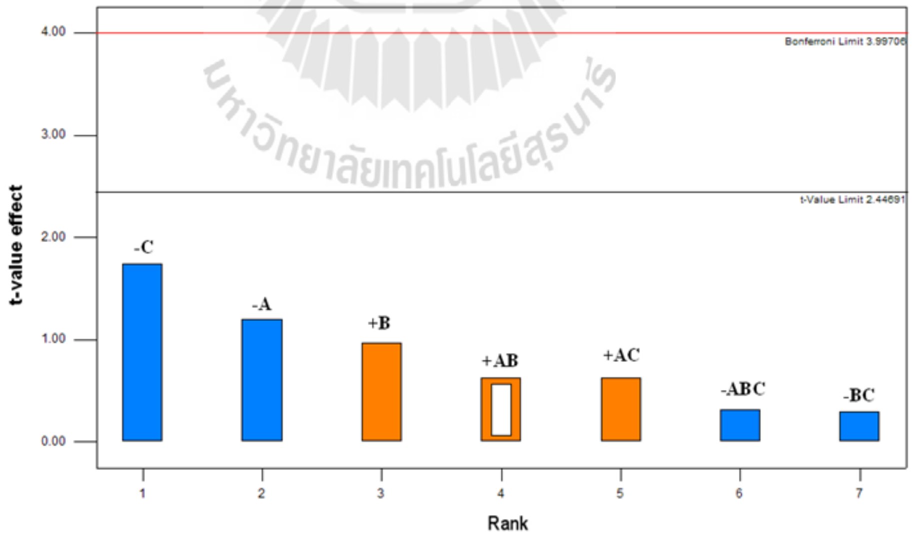


Figure 3.10 Pareto chart analysis of flexural strength of the HDPE/PTFE blends with sauna treatment

Table 3.12 ANOVA test for flexural strength of the HDPE/PTFE blends with sauna treatment

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	0.442	1	0.442	0.390	0.5551
AB	0.442	1	0.442	0.390	0.5551
Residual	6.790	6	1.132		
Cor Total	7.231	7			

The statistical analysis of the flexural modulus of HDPE/PTFE blends before conducting the sauna incubation is performed by the normal plot as presented in Figure 3.11. It is obviously seen that the standardized effect of DCP **(-C)** and interaction between PTFE and silane (**-AB**) are out of the linear trend. Both are negative effects. These two parameters are likely to be the significant effect to the flexural modulus of original blends. The resolution is supported by the pareto analysis shown in Figure 3.12. The bar chart reviews that the computed t-value DCP (**-C)** and interaction between PTFE and silane (-**AB**) are further beyond the critical t-value. It manifests that the parameters are significant effect to the flexural modulus of HDPE/PTFE blend without sauna curing. The ANOVA result, shown in Table 3.13, also indicates that the *p*-values of the model and parameters **C** and **AB** are much below the critical value at 0.05. So, it can conclude that the designed parameters and their content levels used for blending the HDPE/PTFE blends are the significant variable, especially DCP (-**C**) and silane/PTFE (-**AB**), for the flexural modulus of the blends. According to this study, it means that blending HDPE/PTFE with low level of DCP content the flexural modulus of the blends before undergoing sauna curing would be lower that the blend with high level content of DCP. Similarly, blending with high level of silane (+**B**) and low level of PTFE (-**A**) or vice versa, it would result lower in flexural modulus of the blends.

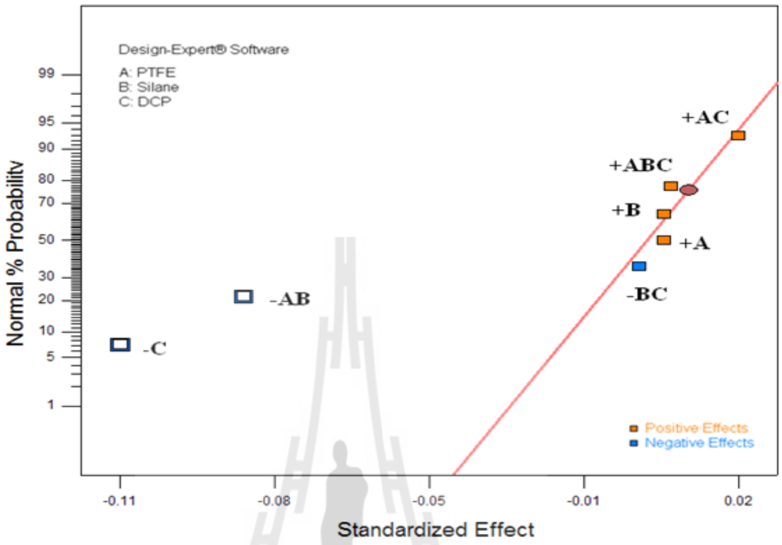


Figure 3.11 Normal probability plot of flexural modulus of the HDPE/PTFE blends without sauna treatment

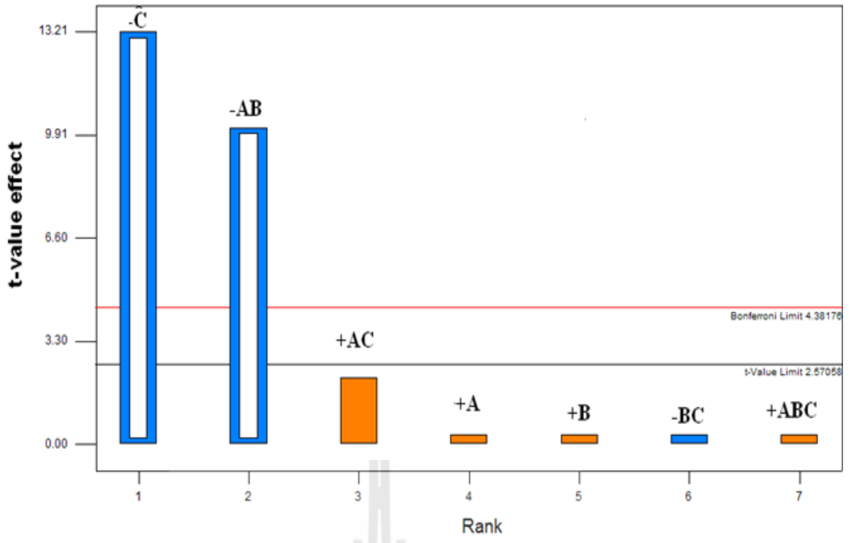


Figure 3.12 Pareto chart analysis of flexural modulus of the HDPE/PTFE blends without sauna treatment

Table 3.13 ANOVA test for flexural modulus of the HDPE/PTFE blends without sauna treatment

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	0.037	2	0.018	138.585	< 0.0001
C-DCP	0.023	1	0.023	174.434	< 0.0001
AB	0.014	1	0.014	102.736	0.0002
Residual	0.001	5	0.000		
Cor Total	0.037	7			

Normal probability plot of the flexural modulus of the sauna cured HDPE/PTFE blends is demonstrated in Figure 3.13. It is seemingly seen that all of the standardized effect values are closely laid in linear trend. However for the sake of the statistical analysis, the highest calculated effect value, and also the most likely among the others, of DCP content **(-C)** was selected for the further computation. Pareto indicator shown in Figure 3.14 is evidenced that DCP (**-C)** is strongly to be significant parameter to have effect on the flexural modulus of the blends. Because, its calculated *t*-value is above the critical value. The argument is confirmed again by ANOVA conclusion as given in Table 3.14. The obtained *p*-values of the experimental model and also DCP parameter are 0.0176 that lower than the assigned critical value at 0.05. It manifests that DCP contents used for blending of HDPE/PTFE has the real significant effect on flexural modulus of the blend sample after sauna incubation. Blending the HDPE/PTFE using low level of DCP content (-**C**) would result the sauna cured blend with lower flexural modulus than the sample using high level of DCP. This statistical conclusion is in agreement with the science aspect. Dicumyl peroxide (DCP) was employed as free radical initiator for grafting vinyl group of silane into the HDPE chain. The more higher in DCP concentration, the higher in grafted points, and hence the more higher in crosslink density via the silane/moisture condensation through the sauna curing process. Generally, macro chains with high crosslink density would behave like thermoset in nature, high in flexural modulus. On the other hand, with lower crosslink density, it would obey the thermoplastic characteristic. Hence, HDPE/PTFE blended with low level of DCP after sauna incubation would have less crosslink density than the blends with high level of DCP added.

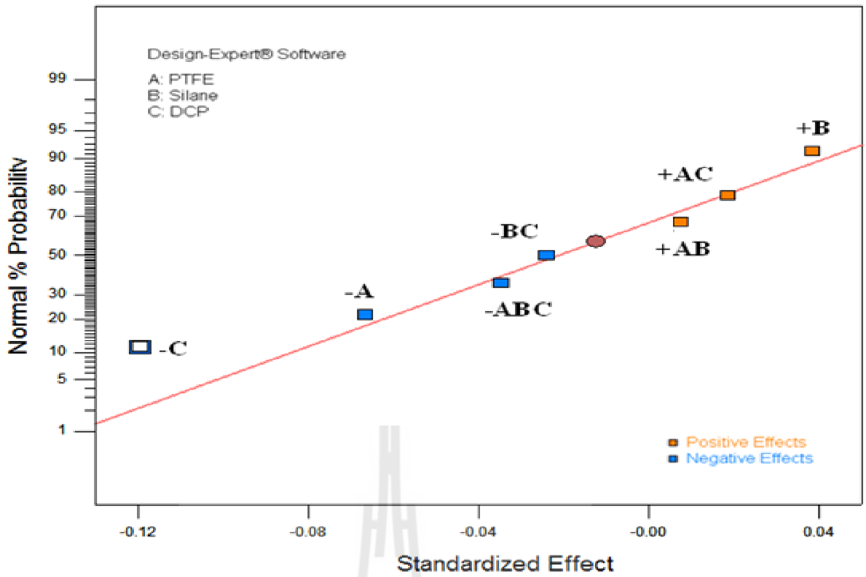


Figure 3.13 Normal probability plot of flexural modulus of the HDPE/PTFE blends with sauna treatment

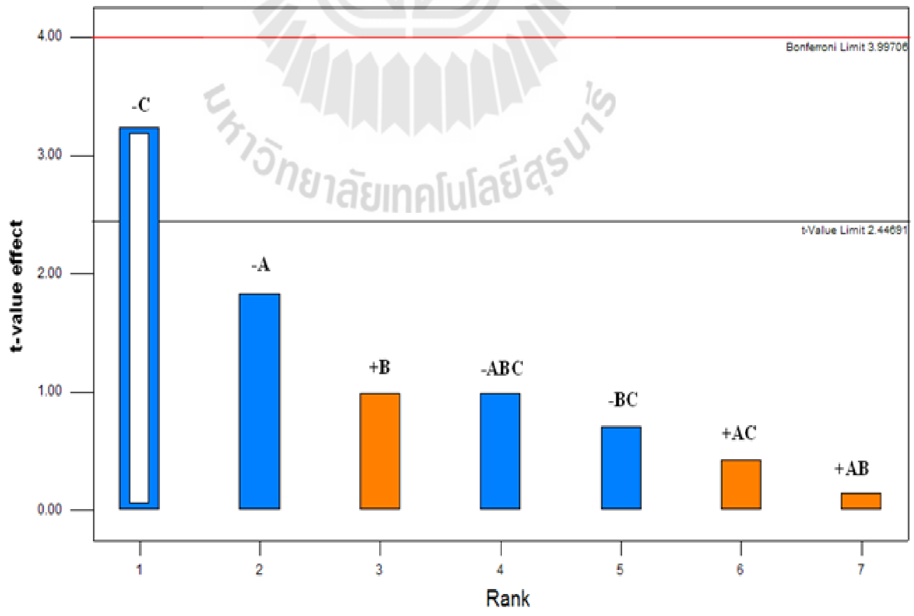


Figure 3.14 Pareto chart analysis of flexural modulus of the HDPE/PTFE blends with sauna treatment

Table 3.14 ANOVA test for flexural modulus of the HDPE/PTFE blends with sauna treatment

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	0.026	1	0.026	10.510	0.0176
C-DCP	0.026	1	0.026	10.510	0.0176
Residual	0.015	6	0.003		
Cor Total	0.042	7			

3.5.3 Analysis of tensile properties

The test values of the tensile properties, both strength and modulus of HDPE blended with PTFE with and without sauna curing are summarized in Table 3.15 respectively. General observation, it is seen that the tensile strength values undergone sauna incubation are slightly higher that the samples without curing as well as the tensile modulus. The slight superiority in the tensile properties after the sauna treatment might be due to either from the silane/water condensation reaction or increasing in the crystallinity of the polymer chains after prolong annealing at temperature slightly above T_g. Taken the statistical analysis into account, Figure 3.16 shows the normal % probability and standardized effect plot of the tensile strength respond of the original blends. It is obviously noticed that interacted parameters between PTFE and DCP contents (+AC) is alighted outside the linear regression line. And, it is also the positive effect. Confirming of the possibility of AC as being the significant effect, the pareto plot given in Figure 3.16 indicates that the t-value of AC is lower than the critical value. It reveals that this interacted parameter is not significant effect to the tensile strength of HDPE/PTFE blend. Strengthen the statement by the ANOVA conclusion shown in Table 3.16, it is seen that the p values of the design model and also the AC are 0.3167 which are above the assigned value at 0.05. It concludes that the designed experiment and also +AC are not significant effect to the tensile strength of the original sample HDPE/PTFE blends.

Table 3.15 Tensile properties of HDPE/PTFE blends

Run	Tensile strength(MPa)		Tensile modulus (GPa)	
	Original	Cured	Original	Cured
1 (+,+,+)	21.16±0.39	22.13±0.55	0.760±0.034	0.846±0.079
2 (+,+,-)	21.80±0.34	22.21±0.32	0.856±0.029	0.808±0.043
3 (+,-,+)	21.44±0.07	21.82±0.06	0.820±0.012	0.808±0.059
4 (+,-,-)	22.03±0.20	22.09±0.31	0.880±0.032	0.860±0.021
5 (-,+,+)	21.71±0.13	21.86±0.22	0.854±0.019	0.828±0.030
6 (-,+,-)	22.45±0.12	22.60±0.25	0.916±0.015	0.862±0.043
7 (-,-,+)	21.45±0.15	22.21±0.20	0.766±0.048	0.828±0.018
8 (-,-,-)	22.14±0.24	22.58±0.19	0.832±0.015	0.858±0.022

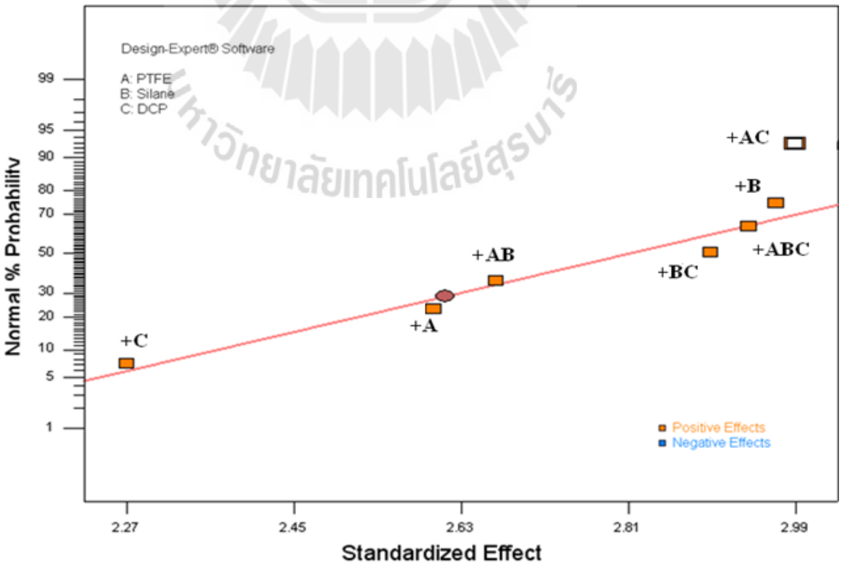


Figure 3.15 Normal probability plot of tensile strength of the HDPE/PTFE blends without sauna treatment

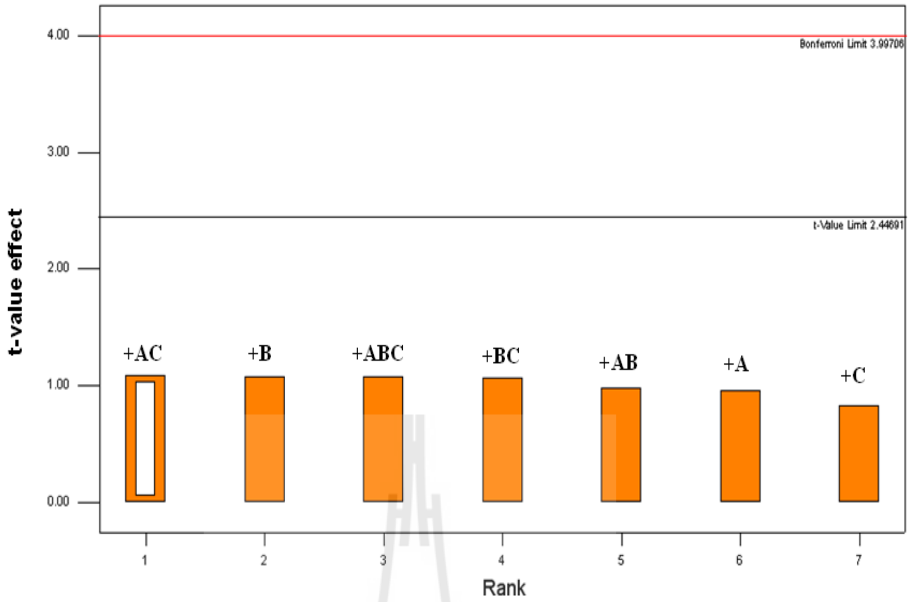


Figure 3.16 Pareto chart analysis of tensile strength of the HDPE/PTFE blends without sauna treatment

Table 3.16 ANOVA test for tensile strength of the HDPE/PTFE blends without sauna treatment

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	17.850	1	17.850	1.192	0.3167
AC	17.850	1	17.850	1.192	0.3167
Residual	89.815	6	14.969		
Cor Total	107.666	7			

Figure 3.17 the normal plot of the tensile strength of HDPE/PTFE blends undergone sauna curing. It is also seen that the positive effect of the interacted parameters PTFE and DCP content (+**AC**) is again excluded from the linear trend. This parameter is suspected to be the significant parameter. Revealing by the pareto

chart, it is confirmed that the calculated *t*-value of +**AC** is far below the critical line. It suggests that this interacted parameter is unlikely to be the significant effect to the tensile strength. According to the statistical analysis by ANOVA, it conclusion is presented in Table 3.17. It is seen that the obtained *p*-values for the designed models and +AC are at 0.3915. It is located within the given degree of confidential, 0.05. Hence, it can conclude that the presence designed experiment and the interacted parameters between PTFE and DCP content (+**AC**) do not have the significant effect to the tensile strength of the sauna cured HDPE/PTFE blend samples.

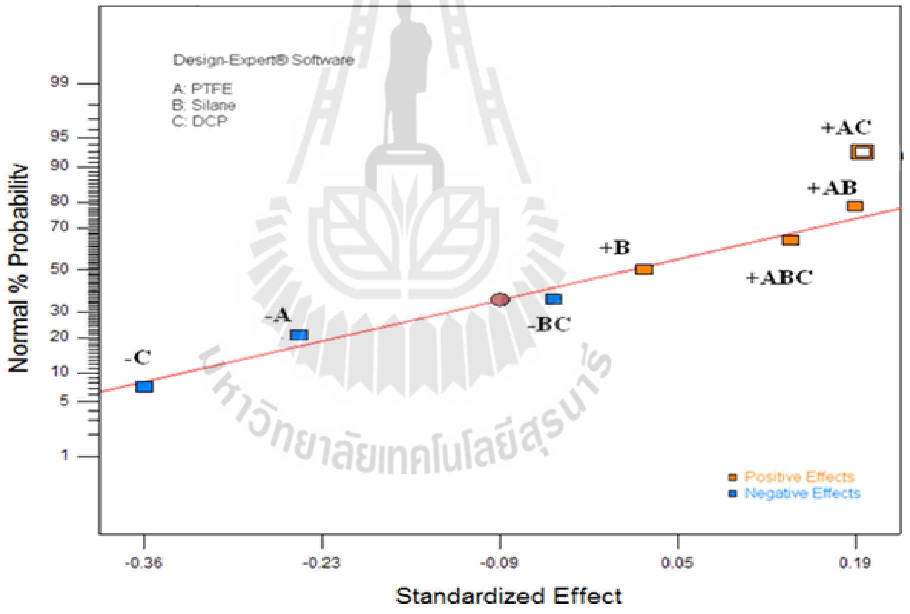


Figure 3.17 Normal probability plot of tensile strength of the HDPE/PTFE blends with sauna treatment

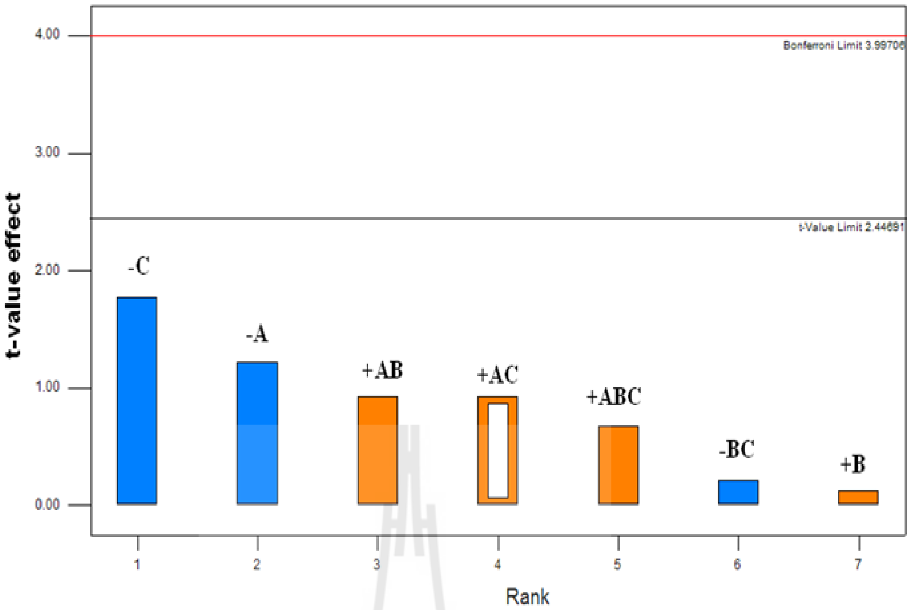


Figure 3.18 Pareto chart analysis of tensile strength of the HDPE/PTFE blends with sauna treatment

Table 3.17 ANOVA test for tensile strength of the HDPE/PTFE blends with sauna treatment

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	0.072	1	0.072	0.853	0.3915
AC	0.072	1	0.072	0.853	0.3915
Residual	0.508	6	0.085		
Cor Total	0.580	7			

The standard normal plot of the tensile modulus of HDPE/PTFE blends tested from the original specimen is shown in Figure 3.19. It is observed that all the calculated standard effects are almost linearly lined, except for the parameter **A**, PTFE content. The PTFE powder could have the significant effect to the tensile modulus of the original sample. A long with the pareto result shown in Figure 3.20, it is undoubtedly noticed that the calculated *t*-value of parameter **A** is much lower than the critical limit line. Also from the ANOVA summarization given in Table 3.18, it is apparently seen that the computed *p*-value of the model and parameter **A**, PTFE content, is 0.7691. The value is far beyond the critical value at 0.05. Taken from the plots and ANOVA conclusion, it is strongly suggested that the given parameters and their levels used in the designed experiment do not have the real significant effect on the tensile modulus of the original HDPE/PTFE blend samples.

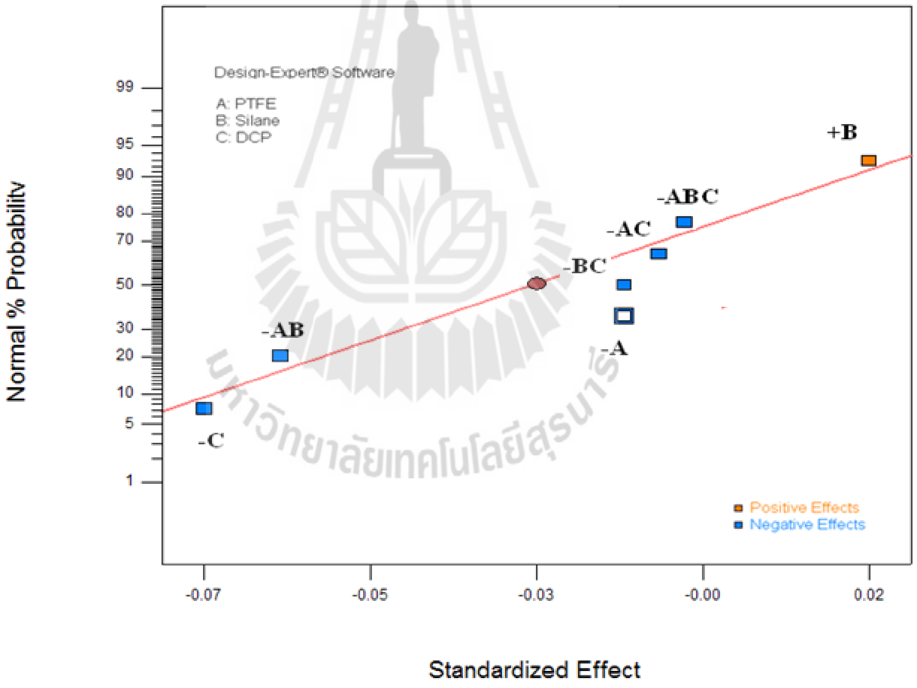


Figure 3.19 Normal probability plot of tensile modulus of the HDPE/PTFE blends without sauna treatment

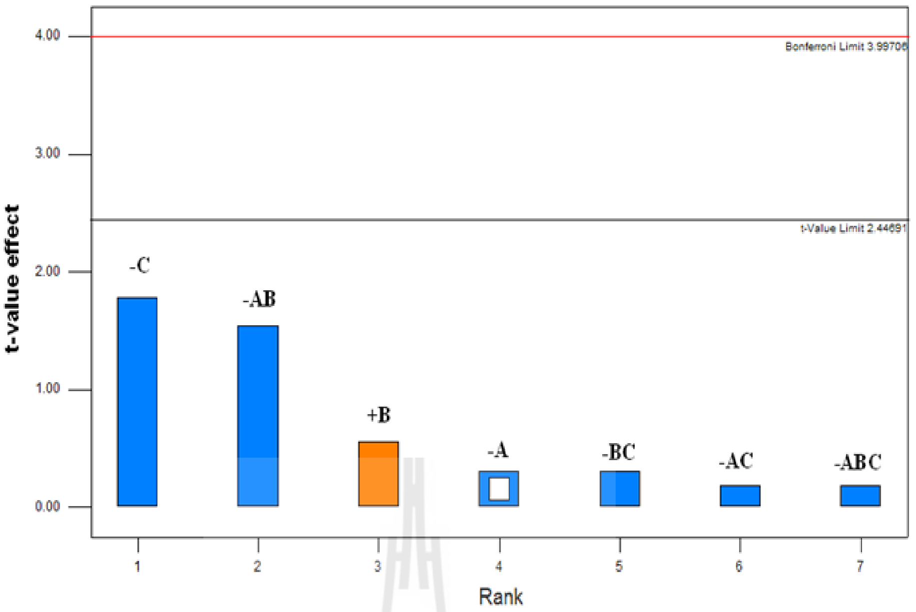


Figure 3.20 Pareto chart analysis of tensile modulus of the HDPE/PTFE blends without sauna treatment

Table 3.18 ANOVA test for tensile modulus of the HDPE/PTFE blends without sauna treatment

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	0.000	1	0.000	0.094	0.7691
A-PTFE	0.000	1	0.000	0.094	0.7691
Residual	0.020	6	0.003		
Cor Total	0.020	7			

For the tensile modulus of HDPE/PTFE blend samples after sauna incubation at 65°C for 12 hours, Figure 3.21 shows the normal plot of the standard effects of the designed parameters. The plot indicates that all of the calculated effect values could be fitted into the linear trend line. For the sake of the statistical analysis, the interacted parameters, +**ABC**, which is slightly further beyond the linear trend, is selected for the computation. According to the statistical computation, the pareto plot of the calculated *t*-value effect was constructed as illustrated in Figure 3.22. It indicates that the *t*-value effect of the interacted parameters, +**ABC**, is lower than the given critical limit line. Again, it manifest that this interacted parameters is not significant effect to the tensile modulus. Final conclusion is performed by the ANOVA analysis. The analysis results are summarized in Table 3.19. It is obvious that the computed *p*-value of the designed models and the ABC parameters is 0.1534, higher than 0.05. Form the statistical results obtained, they are confirmed that the given designed parameters and their levels used in this presence experiment do not have the real significant effect on the tensile modulus of the sauna cured HDPE/PTFE blend sample.

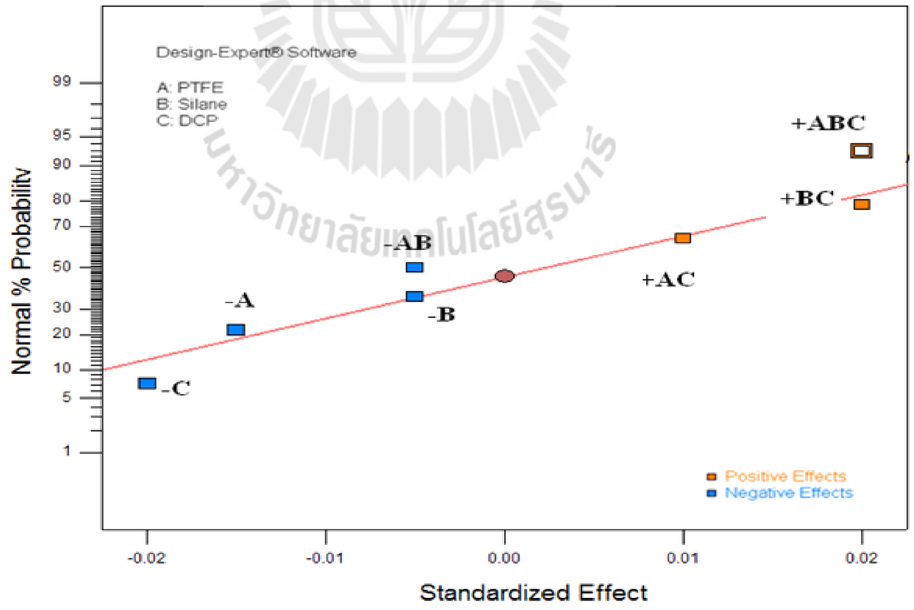


Figure 3.21 Normal probability plot of tensile modulus of the HDPE/PTFE blends with sauna treatment

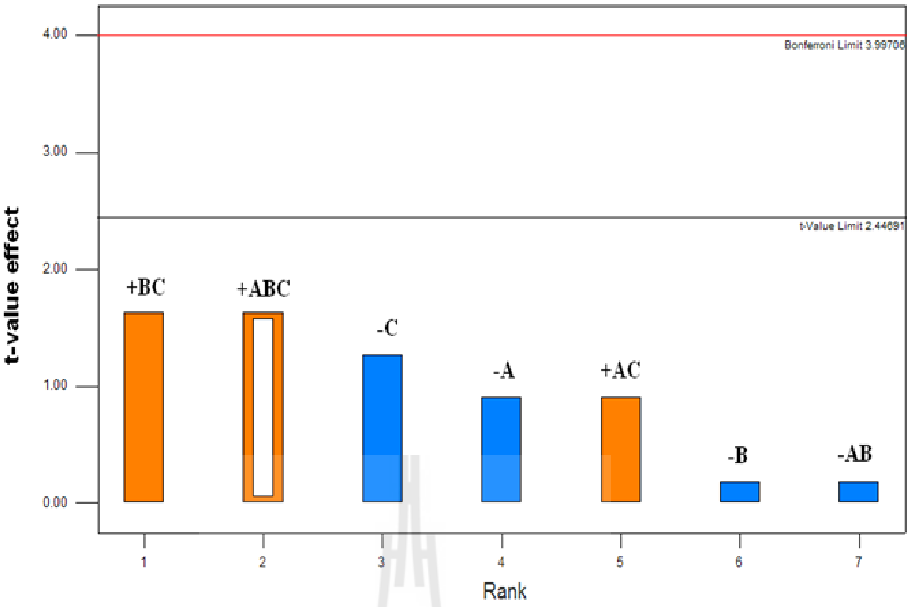


Figure 3.22 Pareto chart analysis of tensile modulus of the HDPE/PTFE blends with sauna treatment

Table 3.19 ANOVA test for tensile modulus of the HDPE/PTFE blends with sauna treatment

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	0.001	1	0.001	2.670	0.1534
ABC	0.001	1	0.001	2.670	0.1534
Residual	0.002	6	0.000		
Cor Total	0.003	7			

3.5.4 Analysis of impact strength

The impact toughness by mean of notched impact strength of HDPE/PTFE blend derived from the design experiment for both original and cured samples are summarized in Table 3.20. The results show that notched impact strength of cured samples is noticeably higher than the values obtained from the original ones. There are two folds explanation. The macro chain crosslink via the silane/water condensation and during the sauna treatment and also the increasing in the crystallinity of the semicrystalline polyolifins during prolong annealing at temperature close to their glass transition temperature. These affects could have the positive effect on the fracture toughness of the blends. However, focusing on the statistical point of analysis, the normal plots of notched impact strength of original sample is presented in Figure 3.23. It is seen that all of the calculated parameters effect are acceptably lined in the linear trend except the interacted effect between PTFE and DCP (+**AC**). This factor effect is obviously out of the linear trend. It is taken as the suspect for the main significant effect to the impact strength. Further analysis using the pareto chart shown in Figure 3.24, it is seen that *t*-values for this parameter, **AC**, is lower than the critical value. It indicates that the interacted parameter between PTFE and DCP(+**AC**) is unlikely to be the significant effect to the impact strength of the original blend sample. The statement is confirmed by the ANOVA testing conclusion that is given in Table 3.21. The final verdict reveals that both *p*-value of the model and the **AC** are 0.9432. They are higher than the given critical value at 0.05. It ensures that the notched impact of the HDPE/PTFE blends without undergoing sauna treatment is not significantly affected by the designed parameters and their level used in the research study.

Table 3.20 Notched impact strengths of the HDPE/PTFE blends

Run	**Notched (KJ/m^2)**	
	Original	Cured
1 (+,+,+)	4.63±0.03	4.84±0.06
2 (+,+,-)	3.27±0.21	3.67±0.12
3 (+,-,+)	2.96±0.04	3.31±0.22
4 (+,-,-)	3.17±0.45	3.22±0.09
5 (-,+,+)	3.05±0.01	3.62±0.88
6 (-,+,-)	3.29±0.32	3.57±0.56
7 (-,-,+)	3.79±0.11	3.22±0.77
8 (-,-,-)	2.56±0.05	3.12±0.12

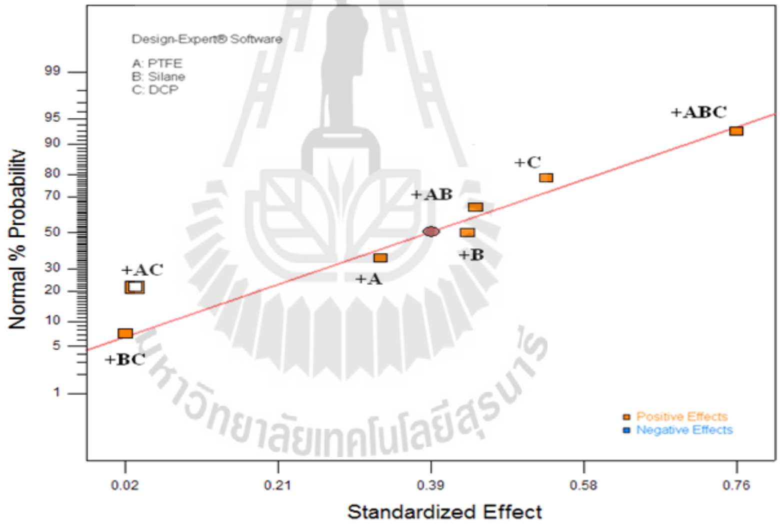


Figure 3.23 Normal probability plot of notched impact strength of the HDPE/PTFE blends without sauna treatment

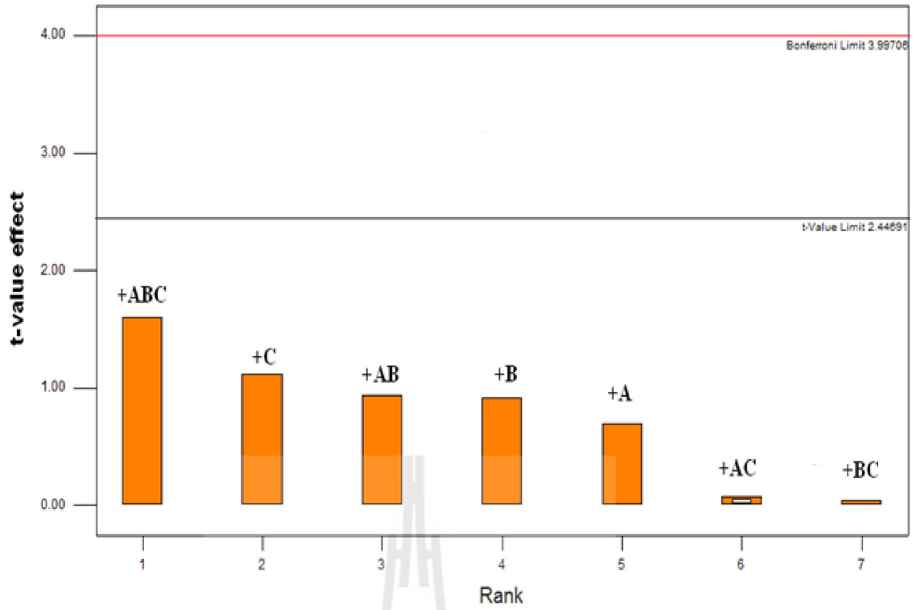


Figure 3.24 Pareto chart of notched impact strength of the HDPE/PTFE blends without sauna treatment

Table 3.21 ANOVA conclusion for notched impact strength of the HDPE/PTFE blends without sauna treatment

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	0.003	1	0.003	0.006	0.9432
AC	0.003	1	0.003	0.006	0.9432
Residual	2.741	6	0.457		
Cor Total	2.743	7			

In case of the samples with sauna treatment, the normal plot is illustrated in Figure 3.25. It obviously seen that the positive effect of silane content (+B) is excluded from the others. The parameter **B** likely to be the pronounce effect to the notched impact of the HDPE/PTFE blends. Surprisingly, the hypothesis is rejected by the pareto outcome shown Figure 3.26. It is apparently seen that the calculated *t*-values of the silane used is below the given critical limit value. The contradiction rejects the normal plot suggestion. It is possible because the rank between highest and lowest effect is comparatively low. Therefore, if they are plotted in the narrow scale x-axis it would lead to miss interpretation. To verify this conflict of observation, the ANOVA analysis is taken into consideration. The result of the ANOVA testing for the impact strength of the sauna cured HDPE/PTFE blends is shown in Table 3.22. The calculated figures are confirmed that *p*-value of experimental model and also for the parameter **B**, silane content, are equally at 0.0617. They are higher than the assigned critical value at 0.05. The analysis is finalized that the designed experiment and the silane content used in this experiment has no significant effect to the notched impact strength of the sauna cured HDPE/PTFE blend samples obtained in this study.

According to the statistical design experiment conducted in this research study, it could declare that DCP, PTFE and silane contents has no significant effect to the notched impact strength of HDPE/PTFE blends regardless to the samples conditioning.

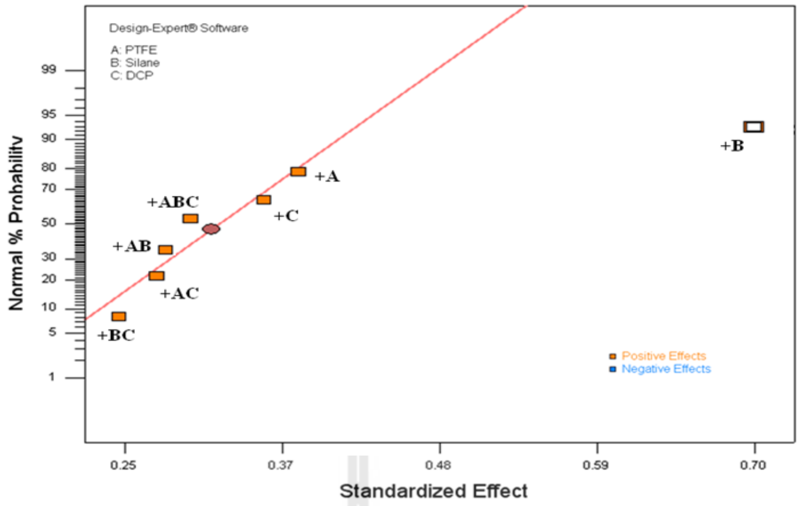


Figure 3.25 Normal probability plot of notched impact strength of the HDPE/PTFE blends with sauna treatment

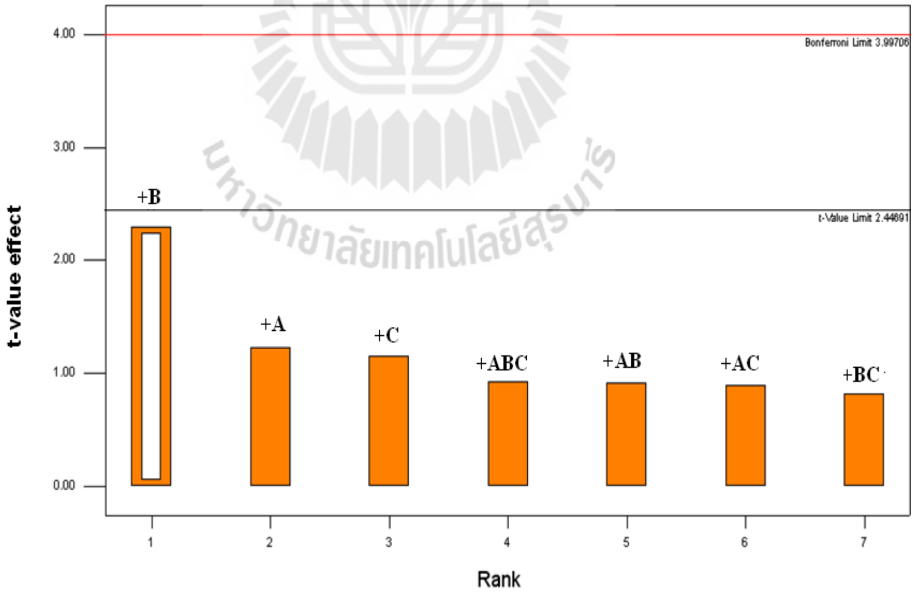


Figure 3.26 Pareto chart of notched impact strength of the HDPE/PTFE blends with sauna treatment

Table 3.22 ANOVA test for notched impact strength of the HDPE/PTFE blends with sauna treatment

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	0.994	1	0.994	5.257	0.0617
B-Silane	0.994	1	0.994	5.257	0.0617
Residual	1.135	6	0.189		
Cor Total	2.129	7			

3.5.5 Analysis of HDT

The service temperature of the HDPE/PTFE blends by mean of heat deflection temperature (HDT) measured at standard load of 445 kPa are reported in Table 3.23 for both original and cured sample, respectively. Similar to those impact results, it is noticed that HDT of sauna cured blends are slightly elevated than the original ones. Again, sauna induced crosslink and increasing in the chain crystallization would be taken into account.

Table 3.23 Heat deflection temperature of HDPE/PTFE blends

Run	**HDT (^{0}C)**	
	Original	Cured
1 (+,+,+)	69.4±1.3	80.5±1.0
2 (+,+,-)	64.8±0.1	71.4±0.0
3 (+,-,+)	65.4±1.3	68.0±1.0
4 (+,-,-)	66.4±1.4	71.0±0.5
5 (-,+,+)	63.4±1.1	66.2±0.7
6 (-,+,-)	66.2±1.6	73.8±1.1
7 (-,-,+)	68.2±1.3	74.6±0.9
8 (-,-,-)	68.6±1.9	78.6±1.1

The statistical analysis by the Design Expert^{TM} is assisted to resolve the effect of the assigned parameters. The standardized effects is plotted against their probability and shown in Figure 3.27 for the original sample. The plot indicates that all the designed parameters are formed the acceptable linear graph. It preliminary indicates that the designed parameters would have no real effect to the HDT of the blends. For the sake of statistical analysis, interacted effect between PTFE and silane content, +**AB,** which is the positive effect to HDT, was taken as suspected to be the significant effect. It is not only shown as the highest calculated effect value but also it is slightly out of the linear trend line. Extent analysis by the Pareto result given in Figure 3.28, guarantees that the designed parameters have no significant effect to the HDT respond because all of the calculated *t*-values are far below the critical limit value. The conclusion is reconfirmed again by ANOVA testing outcome presented in Table 3.24. It is evidenced that the *p*-values of the model and also the suspected parameter, **AB**, are at 0.0976, above the given decisive figure at 0.05. Regarding to the statistical analysis, it reviews that the designed model, both parameters and their levels of contents used in the HDPE/PTFE blend ingredient, has no significant effect to the HDT of the blended samples without sauna incubation.

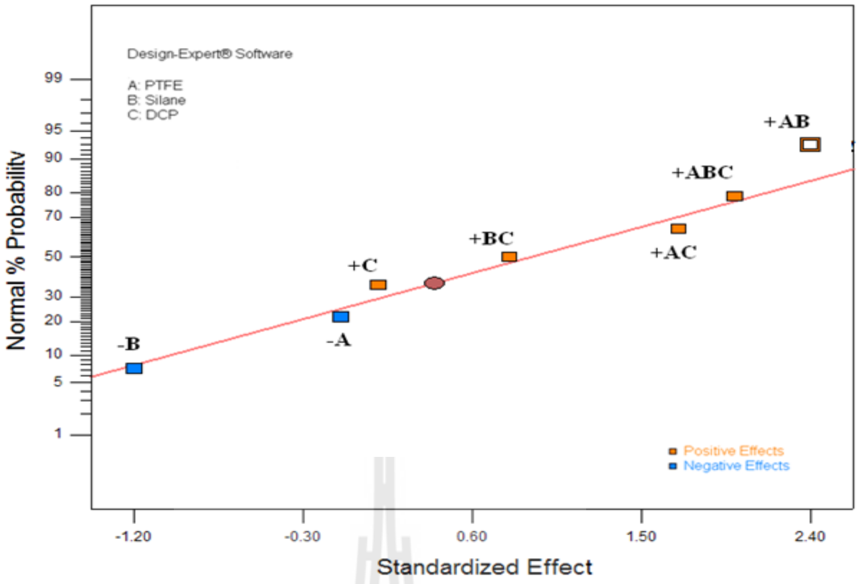


Figure 3.27 HDT normal probability plot of the HDPE/PTFE blends without sauna treatment

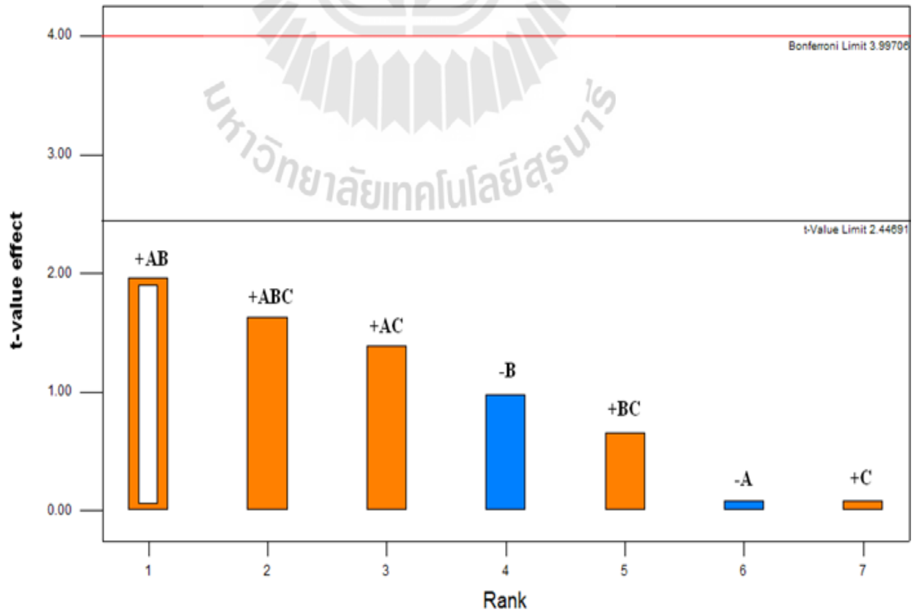


Figure 3.28 Pareto chart of the HDT respond for the HDPE/PTFE blends without sauna treatment

Table 3.24 ANOVA conclusion of the HDT respond for the HDPE/PTFE blends without sauna treatment

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	11.520	1	11.520	3.844	0.0976
AB	11.520	1	11.520	3.844	0.0976
Residual	17.980	6	2.997		
Cor Total	29.500	7			

Standard normal plot of the HDT obtained after sauna curing is presented in Figure 3.29. According to the plot, it is seen that the negatively affect of DCP content (-**C**) shows the highest calculated effect value and also out of the linear trend line to the HDT respond. It indicates that this parameter is possibly to be the significant effect to the HDT of the cured HDPE/PTFE blends. In contradiction resolved from the pareto analysis in Figure 3.30, it is evidenced that the calculated *t*-value DCP content is below the critical *t*-value. It manifests that this parameter has no significant effect to the HDT of cured blends. The conclusion is supported again by the ANOVA result summarized in Table 3.25. The ANOVA figures reviews that the calculated *p*-value of the designed model and also **C** parameter do not have the significant effect to the HDT of HDPE/PTFE blends after sauna curing because the *p*-values, 0.7440, are higher than 0.05.

Hence, regarding to the statistical analysis of the experimental set up in this research work it can say that DCP, silane, PTPE contents at the given levels used do not have significant effect to the HDT of the HDPE/PTFE blends either before or after sauna incubation.

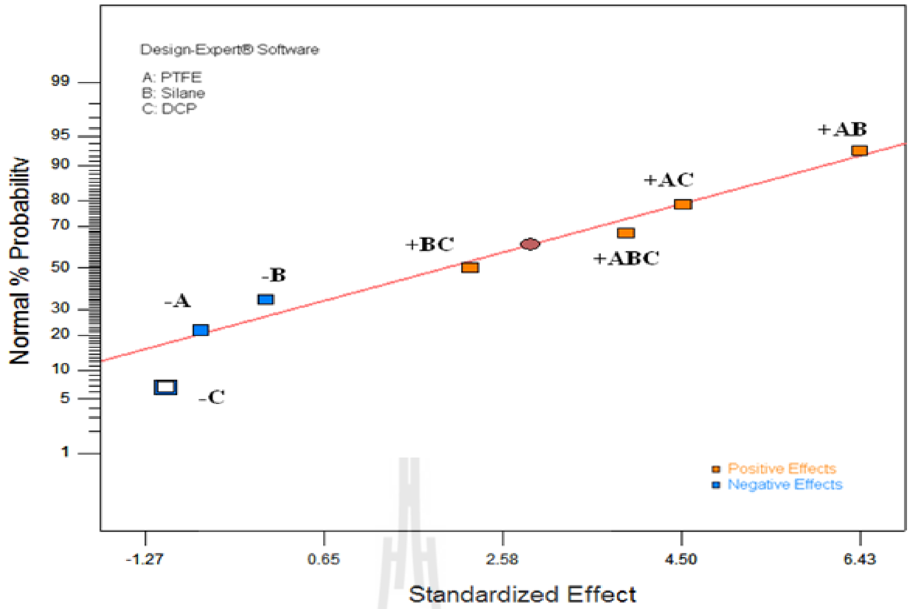


Figure 3.29 Normal probability plot of HDT of samples with sauna treatment

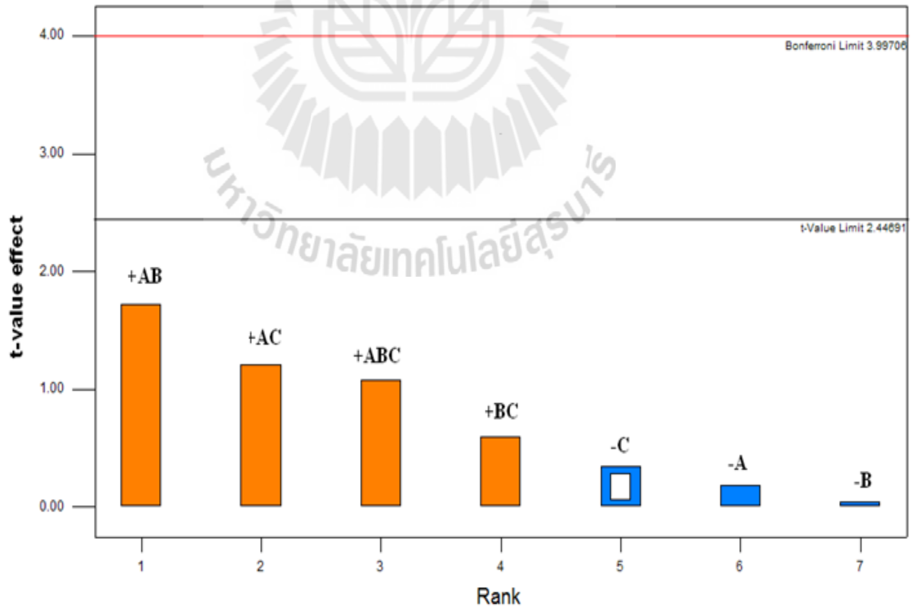


Figure 3.30 Pareto chart of HDT of samples with sauna treatment

Table 3.25 ANOVA test for HDT of samples with sauna treatment

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	3.251	1	3.251	0.117	0.7440
C-DCP	3.251	1	3.251	0.117	0.7440
Residual	166.788	6	27.798		
Cor Total	170.039	7			

3.5.6 Analysis of water drop ratio

Surface tension of the HDPE/PTFE blends was investigated on the film sample by mean of measuring the water drop diameter (D_{sample}). Then it was used to compare with the test result performed in PTFE/Fiber Glass sheet (D_{PTFE}) as the ratio value (D_{sample}/D_{PTFE}). If the ratio value less than 1.0, $D_{PTFE}>D_{sample}$, it means that the sample has poorer surface adhesion to water than PTFE sheet. It would be good for the low surface adhesion container application such as the cup for harvesting the natural rubber latex.

The test values of the ratio of the original and sauna cured are summarized in Table 3.26. From the values obtained it seen that the ratio derived from the original HDPE/PTFE sheets are higher than 1.0. However, testing on the sheet after sauna incubation, the result indicates that the ratios of Run#1 and Run#7 are noticeably less than 1.0. If the measured result is corrected and repeatable, it would indicate that the blends formula have possibility to be used as low surface tension material and higher processability than PTFE. But, it is awkward to see such result because Run#1 and Run#7 were derived from the formula having low (-) and high (+) PTFE content. According to the preliminary outcome, it reviews that the surface tension of the blends does not depend on the PTFE. However, further statistical analysis will be discussed.

The normal and pareto plots for the effect analysis of the designed parameters on the D_{sample}/D_{PTFE} ratio of the HDPE/PTFE sheet without sauna curing are presented in Figure 3.31 and 3.32, respectively. From the effect plot, it seen that the highest negative effect of PTFE content (**-A**) is located outside the linear trend line. It is suspected to be the significant effects to the water drop diameter ratio respond. Vice versa, the pareto indicator shows that the calculated *t*-value of **A**-parameter is below the critical one. It strengthens that the level of PTFE used for blending with HDPE in this research work would not have the real effect to the surface tension of the blends. The statement is confirmed by the ANOVA conclusion given in Table 3.27. The calculated *p*-values of the model and also **A**-parameter are at 0.7807, that are higher than the critical value at 0.05. Therefore, statistical conclusion can be made that the assigned parameters and their levels used for blending in this research study do not have statistically effect to the surface property measured by the water drop diameter ratio on the HDPE/PTFE blends sheet before undergoing sauna incubation.

Table 3.26 D_{sample}/D_{PTFE} ratio of HDPE/PTFE blends sheet without and with sauna treatment

Run	D_{sample}/D_{PTFE}	
	Original	Cured
1 (+,+,+)	1.25±0.01	0.98±0.02
2 (+,+,-)	1.17±0.01	1.16±0.01
3 (+,-,+)	1.23±0.04	1.07±0.01
4 (+,-,-)	1.14±0.02	1.01±0.02
5 (-,+,+)	1.20±0.01	1.01±0.02
6 (-,+,-)	1.26±0.01	1.08±0.02
7 (-,-,+)	1.15±0.02	0.89±0.01
8 (-,-,-)	1.22±0.01	1.06±0.01

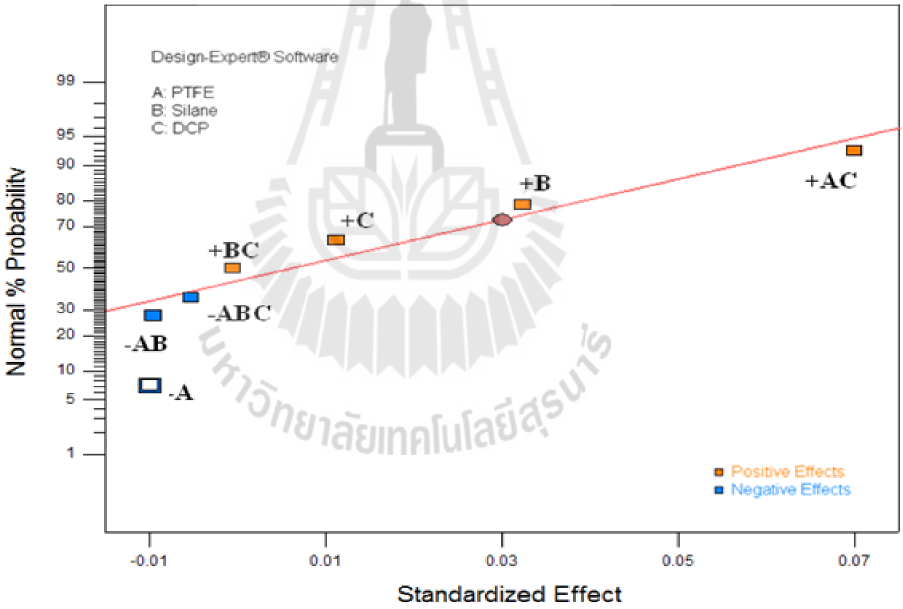


Figure 3.31 Normal probability plot of the D_{sample}/D_{PTFE} ratio respond for the original HDPE/PTFE blends sheet

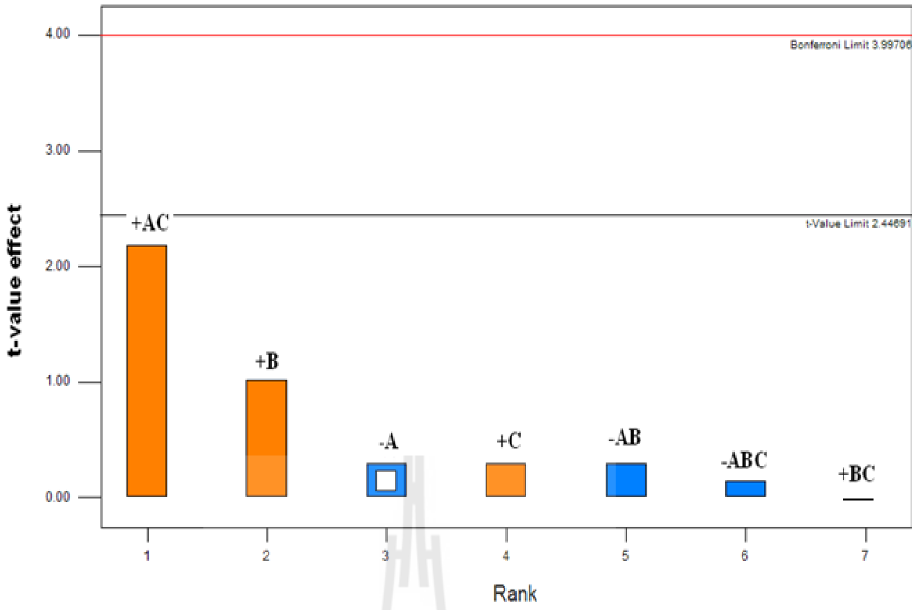


Figure 3.32 Pareto chart of the D_{sample}/D_{PTFE} ratio respond for the original HDPE/PTFE blends sheet

Table 3.27 ANOVA conclusion for the D_{sample}/D_{PTFE} ratio respond for the original HDPE/PTFE blends sheet

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	0.000	1	0.000	0.085	0.7807
A-PTFE	0.000	1	0.000	0.085	0.7807
Residual	0.014	6	0.002		
Cor Total	0.014	7			

For analysis of D_{sample}/D_{PTFE} of the sample undergone sauna treatment, the normal plot of the standardized effect is illustrated in Figure 3.33. The similar consequences to those cured samples observed, acceptable linear trend. The interaction of all parameters (**-ABC**) show the tendency to be the significant and negative effect to the water drop diameter ratio of the HDPE/PTFE blends. Because it is excluded from the others point. For the sake of the statistical conclusion, both pareto and ANOVA results have to be taken into account. The pareto chart, given in Figure 3.34. Reviews that, the calculated *t*-value all factors including **ABC** are below the critical *t*-value. It indicates that the effects are not significant effect to the ratio of the cured blend samples. The conclusion is also strengthened by the ANOVA conclusion at 95% degree of confidential summarized in Table 3.28. It is demonstrated that the experimental model and the interacted parameters **ABC** have no significant effect to ratio between D_{sample} and D_{PTFE} of HDPE/PTFE blends after performing the moisture incubation at 65°C. Because of the computed *p*-values, 0.1417, are above the set value, 0.05.

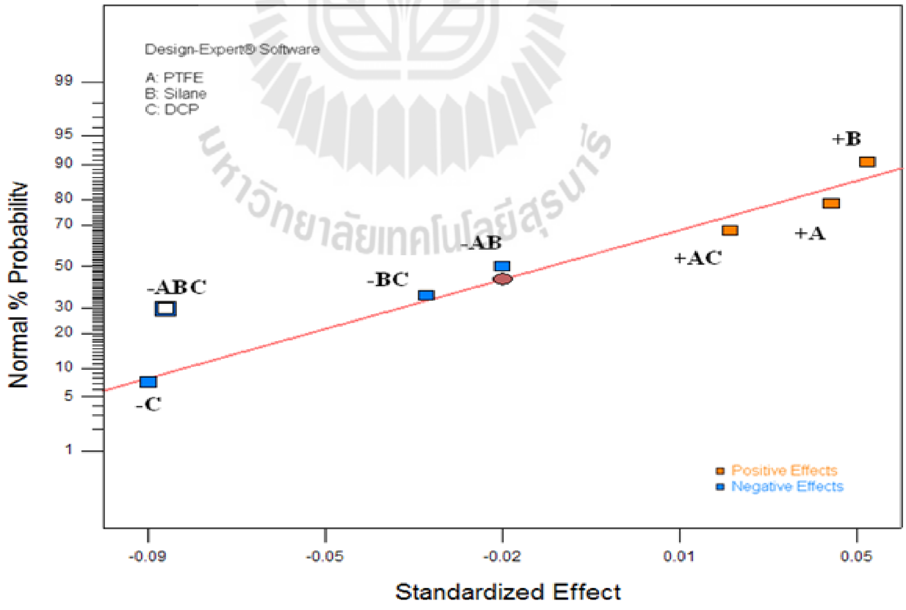


Figure 3.33 Normal probability plot of water drop diameter of the HDPE/PTFE blends with sauna treatment

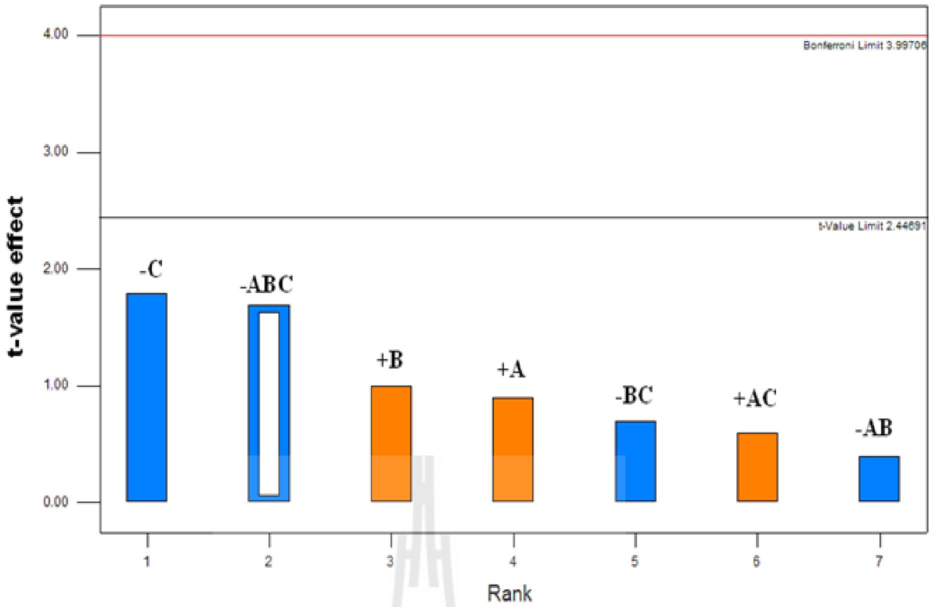


Figure 3.34 Pareto chart of water drop diameter of the HDPE/PTFE blends with sauna treatment

Table 3.28 ANOVA test for water drop diameter of the HDPE/PTFE blends with sauna treatment

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	0.014	1	0.014	2.861	0.1417
ABC	0.014	1	0.014	2.861	0.1417
Residual	0.030	6	0.005		
Cor Total	0.045	7			

Taken both original and cured blend sample, the measurement of the surface tension by mean of calculating the ratio of the water drop diameter on the surfaces of HDPE/PTFE blend films and of the PTFE, the statistical outcome suggested that the parameters and their levels of content used in the blend ingredient conducted in this study have no statistical significant effect to the film surface of the blends.

3.5.7 Statistical analysis of wear resistance

PTFE, without the proper treatment, is known as low surface adhesion to any matrix. There is worth to investigate the adhesion between those two polymers by measurement the wear resistibility of the blends. The abrasion resistance test values, conducted on the film, by mean of measuring the % weight loss for both original and cured blend samples are summarized in Table 3.29. Evidently, the scattered results are observed. There is also having no obvious trends between original and cured samples.

The normal standard effect plot for the % weight loss of HDPE/PTFE blends before undergoing sauna curing process is given in Figure 3.35. It is seen that all of effect points can be acceptably lined and fitted as the linear trend line except for the effect value of the interacted parameters between PTFE and silane content (-**AB**) which is slightly gone beyond the line. For the sake of the software analysis, this point was taken into the calculation for further reinforcing investigation. The analysis result given by pareto plot, Figure 3.36, agrees that the interacted parameters **AB** more likely to be non-significant effect to the wear resistance of the blends. Because the calculated *t*-value obtained from the analysis is below the given limited value. The confirmation of the statement is also signified by ANOVA conclusion shown in Table 3.30. It is seen that *p*-values of experimental design and the interacted between PTFE and silane content are 0.1678. They are above the decisive value at 0.05. So according to the statistical found out, it is strongly suggested that the designed parameters and their levels used in this statistical study have no significant effect to the wear resistance measured by film % weight loss of the HDPE/PTFE blends without sauna curing.

Table 3.29 % weight loss of the HDPE/PTFE blends film

Run	**Weight loss (%)**	
	Original	Cured
1 (+,+,+)	0.42±0.20	0.53±0.18
2 (+,+,-)	0.41±0.08	0.46±0.06
3 (+,-,+)	0.54±0.06	0.37±0.24
4 (+,-,-)	0.54±0.14	0.56±0.11
5 (-,+,+)	0.36±0.14	0.35±0.09
6 (-,+,-)	0.56±0.11	0.37±0.15
7 (-,-,+)	0.29±0.05	0.37±0.04
8 (-,-,-)	0.49±0.06	0.45±0.18

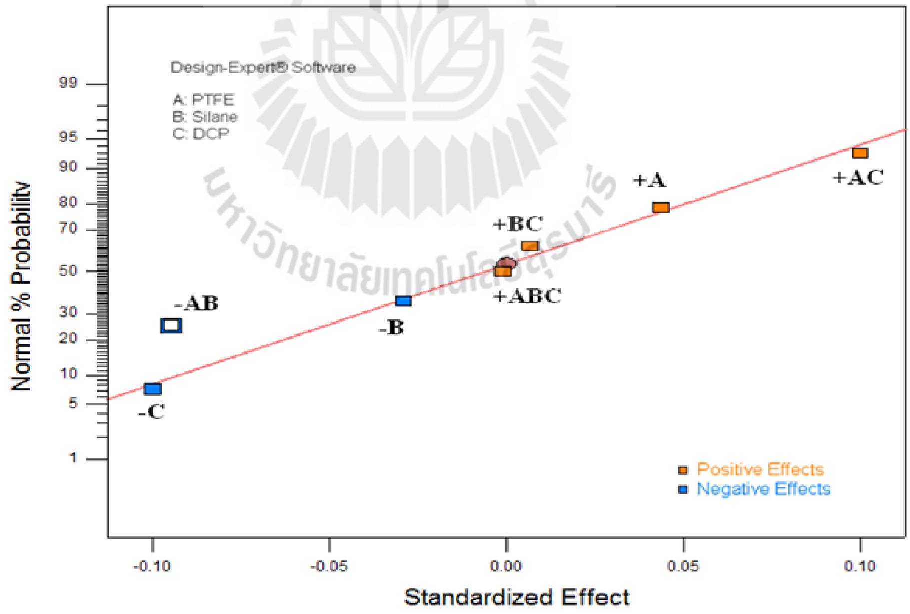


Figure 3.35 Normal probability plot of % weight loss of the HDPE/PTFE blends film without sauna treatment

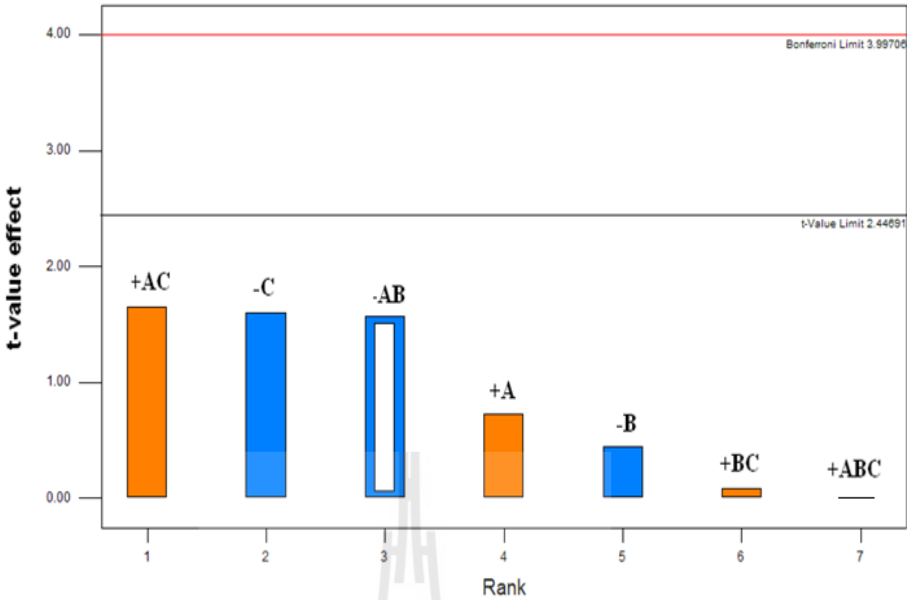


Figure 3.36 Pareto chart of % weight loss of the HDPE/PTFE blends film without sauna treatment

Table 3.30 ANOVA conclusion of % weight loss of the HDPE/PTFE blends film without sauna treatment

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	0.019	1	0.019	2.460	0.1678
AB	0.019	1	0.019	2.460	0.1678
Residual	0.047	6	0.008		
Cor Total	0.067	7			

In case of the blends film undergone sauna treatment, the standard normal plot is presented in Figure 3.37. It is noticed that the similar trend to the original sample is observed. Again, by taken the PTFE content (+**A**), which is not only shown the highest effect value but also it is slightly excluded from the others, as the suspected parameter for analyzing. The result indicated by the pareto chart in

Figure 3.38 shows that the computed *t*-value of this parameter and also the rest are below the limited line. It reveals that the PTFE content is unlikely to be the significant effect to the % weight loss of the sauna cured samples. Further conclusion given by the ANOVA numbers summarized in Table 3.31 reviews that the model, the designed parameters and their level of contents, and amount of PTFE blended are not significant effect to the wear properties measured by % weight loss of the cured HDPE/PTFE films. Because of the concluded *p*-value is equal to 0.0985. This numbers are higher than the critical *p*-value.

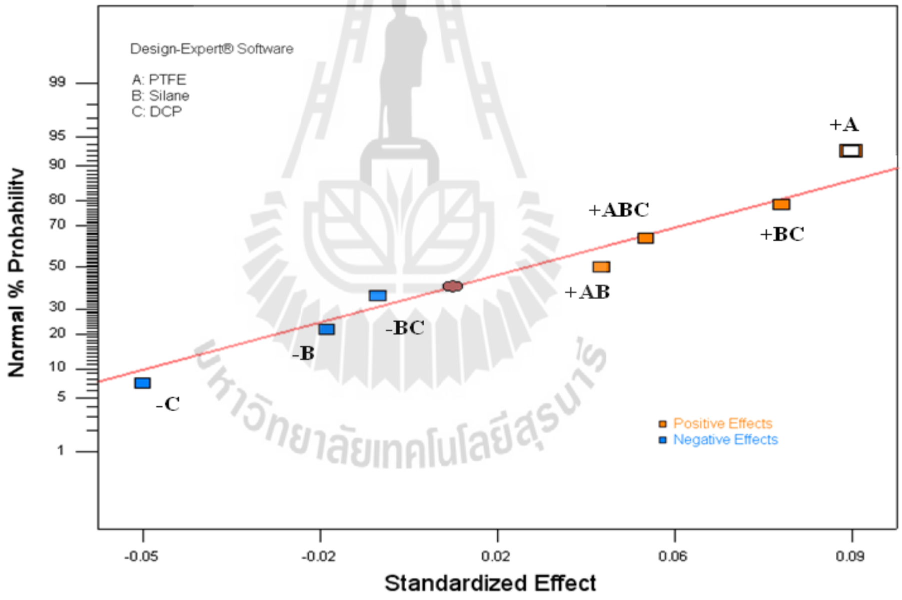


Figure 3.37 Normal probability plot of abrasive resistance of samples with sauna treatment

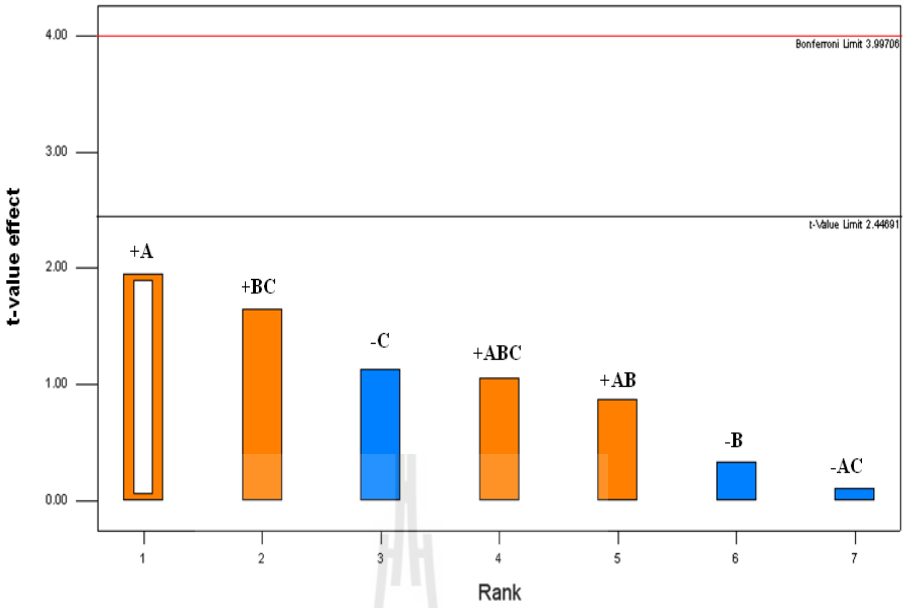


Figure 3.38 Pareto chart of abrasive resistance of samples with sauna treatment

Table 3.31 ANOVA test for abrasive resistance of samples with sauna treatment

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	0.017	1	0.017	3.819	0.0985
A-PTFE	0.017	1	0.017	3.819	0.0985
Residual	0.027	6	0.005		
Cor Total	0.045	7			

The statistically results suggested that the parameters and their assigned contents used for blending HDPE/PTFE in this research study had no real effect the wear property by mean of % weight loss of the film samples both original and sauna cured.

Regarding to the statistical conclusion mentioned above for all the respond properties, the statistical models, or the equation relationship between the levels (+ and -) of the significant parameters and the value of the responds properties can be constructed. According to this experiment, the model equations are given in Table 3.32. It is concluded that only the rheological properties by mean of melt flow index and flexural properties are affected by the given parameters. For the utilization of the equation, it is seen that the MFI relationship of the original blends is given as +4.490-3.240(**C**)-1.870 (**AB**). It refers that if the high flow index of the blend is required, the DCP content (**C**) used must be kept at low level and the contents of PTFE (**A**) and silane (**B**) either at low and high levels (-**A** x +**B** = -**AB**) or vice versa (+**A** x –**B** = -**AB**). The similar manner will apply for prediction of the others respond that are significantly affected by the designed parameters. This preliminary conclusion will be used for further improvement of the properties of HDPE/PTFE blends throughout this study.

Table 3.32 The predicted regression model for properties of HDPE/PTFE blends derived from ANOVA conclusion

Test	Regressed models (original)	Regressed models (sauna cured)
MFI	+4.490-3.240(C)-1.870(AB)	-
Flexural strength	+33.050-0.430(C)+0.350(AC)	No significant
Flexural modulus	+1.593-0.053(C)-0.041(AB)	+1.703-0.058(C)
Tensile strength	No significant	No significant
Tensile modulus	No significant	No significant
Impact strength	No significant	No significant
HDT	No significant	No significant
Dsample /D PTFE	No significant	No significant
Weight loss (%)	No significant	No significant

3.5.8 Morphology observation

The SEM photographs to observe the morphological evidences of the fractured surface of the HDPE/PTFE blend are illustrated in Figure 3.39 (***a***) to 3.39 (***d***) before and after undergoing sauna incubation. They were obtained from the fractured impact specimen of the blends formulated in Run#1 and#8, respectively. These two blends formula represent the blends having the ingredient of the parameters at all low levels (-, -, -) and all high levels (+, +, +) of the contents used, respectively. It is seen in the Figure 3.39 (***a***) and 3.39 (***b***) for the all low levels blends, Run#1, that the PTFE particles are well dispersed throughout the HDPE matrix. It is also obviously observed the space between the particles and the matrix indicating poor surface adhesion between those two polymers. The sauna treatment of the blend, Figure 3.39 (***b***), is proved to be unable to improve the interfacial adhesion between the polymers. For the blend using high level of all parameters content, Run#8, as given in Figure 3.39 (***c***) and 3.39 (***d***), it is also noticed that the gap between the dispersed phase and the matrix is still visible. There is still no surface adhesion improvement via the incubation. However, when compare the fractured surface of the samples between Run#1 and Run#8 the obvious different is that the spider web like surface of the Run#8's blend but less seen in Run#1. This web surface would resolve from the high chain length formed or, perhaps macro crosslink chain, of HDPE via the addition of vinyl silane and DCP crosslink system. Normally, the degree of chain extension or crosslinking would be increased after the silane/moisture induced crosslink via the moisture incubation. The chain extension or crosslinking would cause the change in the blend properties, typically increasing in the properties as indicated from the previous discussion. Granting from this SEM find out, it would say that the adhesion between HDPE and the dispersed particle PTFE is relatively poor. Adding the vinyl silane/DCP crosslink system into the blend ingredient does not improve the surface adhesion between those two polymers. However, macro chain crosslink formation of the HDPE matrix via the silane/peroxide addition does generally help to improve the mechanical properties of the blends.

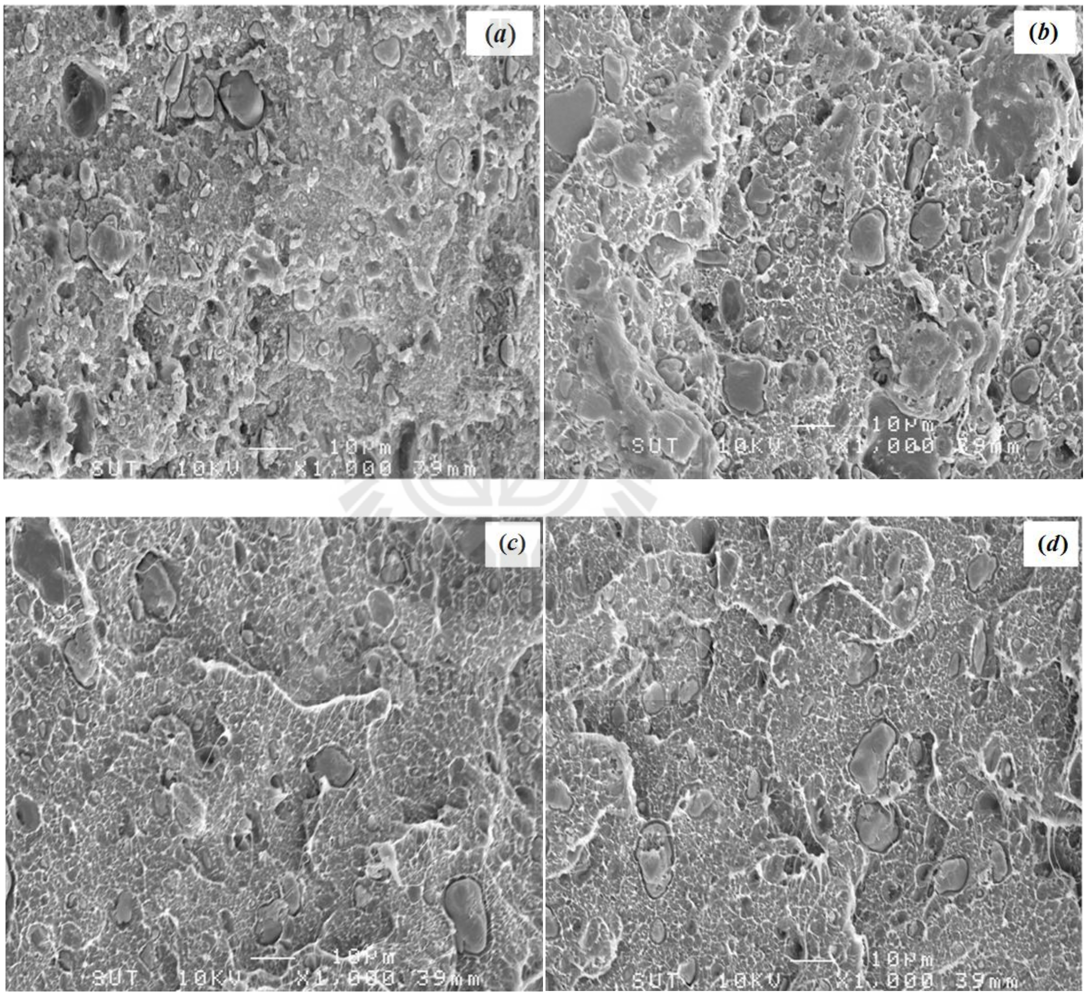


Figure 3.39 SEM micrograph of (***a***) Run.1 original, (***b***) Run.1 cured, (***c***) Run.8 original, (***d***) Run.8 cured (X1000)

3.6 Conclusion

The macro chain crosslink via the silane/water condensation and during the sauna treatment and also the increasing in the crystallinity of the semicrystalline HDPE during prolong annealing at temperature close to their glass transition temperature was taken into account for explaining the slightly increase in the properties of HDPE/PTFE blends. Form the statistical analysis results, using DOE approach, obtained reviewed that the DCP content (**-C**) and interaction amount between PTFE and silane (**-AB**) used for manufacturing of HDPE/PTFE blend had negatively and significantly affected to the flow index of the HDPE/PTFE blend. While, DCP content was negative and significant effect (**-C**) to the flexural strength of the original blend samples. On the other hand, all of assigned parameters and their levels do not have the significant effect to the flexural strength of the HDPE/PTFE blends underwent sauna treatment. For the flexural modulus of HDPE/PTFE blends, the DCP (-**C**) and silane/PTFE (-**AB**) were the significant variable to the property of the original samples. Especially, the DCP (-**C**) was the negative and significant influence to the flexural modulus of the cured samples. Considering on the statistical results obtained, they were confirmed that the given designed experimental parameters and their levels used in this study did not have the real significant effect on the tensile properties of the original and sauna cured HDPE/PTFE blend to the statistical design experiment conducted in this research study. It also could declare that DCP, PTFE and silane contents had no significant effect to the notched impact strength of HDPE/PTFE blends regardless to the samples conditioning. Regarding to the experimental set up in this research work, it suggested that DCP, silane, PTPE contents at the given levels used did not have significant effect to the HDT of the blends. Taken both original and cured blend samples, the measurement of the surface tension by mean of the ratio between the water drop diameter on the HDPE/PTFE blend films and on the PTFE, the statistical outcome suggested that the parameters and their levels of content used in the blend ingredient conducted had no statistical significant effect to the film surface of the blends. Finally, the results indicated that the parameters and their contents used for blending HDPE/PTFE had no influence to the wear property of the film samples. This preliminary conclusion will be used for further improvement in the properties of HDPE/PTFE blends throughout this study.

3.7 Reference

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CHAPTER IV

EFFECT OF SILANE AND TREATMENT OF PTFE ON THE PROPERTIES OF CROSSLINKED HDPE/PTFE BLENDS

4.1 Abstract

The peroxide initiated vinyl silane and moisture induced crosslinked HDPE/PTFE was studied. The effects of silane content varied from 2.0, 2.5, 3.0, 3.5 and 4 phr on the properties of the HDPE/PTFE blends were investigated. Increasing the silane ratio in the silane/DCP crosslink system added into the HDPE/PTFE blends, the test results showed that the MFI of the blends did not increase with increasing the silane coupling agent. The HDT of the original samples were also decreased with increasing the silane loading but after undergoing the sauna treatment the HDT was slightly increased with more of silane added. However, at the given amount of silane, the HDT of the cured sample was significantly higher than the original sample. For the mechanical properties of HDPE/PTFE, the results were reviewed that that more flexible material, or softer, were found when increasing the silane content. The tensile properties were decreased with increasing the amount of the silane. On the other hand, the impact strength of the blends was higher, softer material, when the silane used was increased. The dilution effects from the liquid silane were taken into the explanation for the mechanical properties dependency of the silane. The surface tensions of the

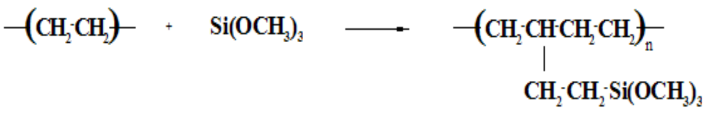
film samples did not depend on the amount of silane added. The surface tension, investigated by the water drop diameter ratio, was almost constant for all samples. The superior in the wear of the samples was found after the sauna treatment at 65^{o}C for more than 12 hours.

In the experiment to investigate the effect of temperature on the surface treatment of PTFE by the free radical decomposed from DCP before blending with HDPE, the results concluded that treatment temperatures, 100^{o}C, 120^{o}C, 130^{o}C and 150^{o}C, of PTFE did not have the significant effect on the mechanical properties what so ever on the HDPE/PTFE blend. However, according to the investigation, the surface of PTFE was noticed to be enhanced when comparing with the surface of PTFE without the treatment. Better in the interfacial adhesion between HDPE matrix and treated PTFE were evidenced.

4.2 Introduction

Crosslinking of polyolefins might improve their high temperature properties and extend their applications. Silane crosslink system, with the assisting of the free radical induced grafting, uses a siloxane bridges to link polyethylene molecules. There are a few variations to achieve silane crosslinking such as reactivity of vinyl groups on the molecule and stability of the generated free radical. The chemistry of this method is illustrated in Figure 4.1

Step 1 PE + Silane + Peroxide



Step 2 Hydrolysis: catalyst, H_2O

Step 3 Condensation: catalyst

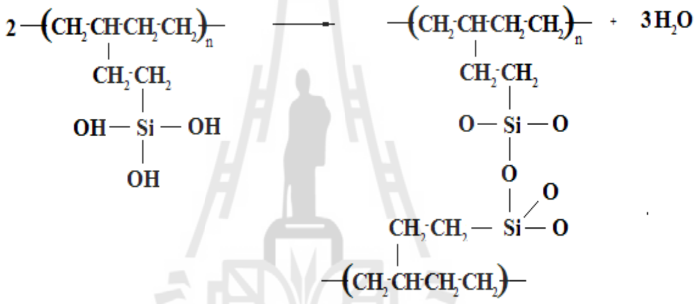


Figure 4.1 Chemical reaction of silane crosslink technique

The first step is the grafting of the chemical silane onto the polymeric chain to form vinyl silane copolymer. Peroxide agent again will initiate the reaction at elevated temperature and form free radicals. Free radicals of peroxide agent will abstract hydrogen from the polyethylene molecules, thus creating unstable carbon (step 1 of Figure 4.1). After which, silane is grafted onto the carbon atom to form a copolymer and the remaining free radical on the copolymer branch will continue to abstract a hydrogen atom.

This abstraction of hydrogen to form a stable copolymer further propagates the action of the silane grafting. At this stage, the copolymer still remains as thermoplastic that can be processed as any thermoplastic could. The resulting of copolymer is put into the converters to form the finished product. For example, pipes or cables.

The next step requires the finished product to be cured (i.e. converting the grafted copolymer into a crosslinked network) using moisture as an active reagent. The curing involves hydrolysis and condensation reaction, which results in a molecule of water being generated, which in turn initiates another curing reaction (step 3 of Figure 4.1). This reaction continues until all the grafted copolymer is converted to cross link chains.

Kalyanee Sirisinha, Marnviga Boonkongkaew and Soontaree Kositchaiyong reported High-density polyethylene (HDPE) was melt-grafted with vinyl trimethoxysilane using dicumyl peroxide as initiator. Three types of ethylene copolymers were used as silane carriers, and were evaluated for their ability to assist the silane-grafting and water crosslinking of HDPE. FTIR revealed that an increase in the amount of silane absorbed in the carriers did not help improve the silane-grafting efficiency. However, the gel and rheological results showed that those carriers promoted the rate of crosslinking and increased the density of the crosslink network. Ethylene vinyl acetate showed a stronger effect in this respect than ethylene octene and ethylene-butene copolymers. Analysis of the crosslinked materials by heat distortion temperature (HDT) test and thermogravimetric analysis (TGA) indicated a marked increase in distortion and decomposition temperatures, as well as thermal activation energy, compared to the neat HDPE. The presence of silane crosslink also resulted in a slight improvement in tensile yield stress and modulus.

In this report, the blend between HDPE/PTFE in the present of silane/peroxide crosslink system was performed and being discussed. One of the main research objectives is the improvement surface adhesion between the HDPE/PTFE by either by the chemical interaction and mechanical inter locking.

4.3 Research methodology

4.3.1 Materials and chemical reagents

High density polyethylene (HDPE, EL-Lene H5814J), is the general purpose high density polyethylene resin that suitable for injection molding process. It was used as the main polymer matrix. This processing graded HDPE has good flow ability and design for high productivity with good toughness product. It is kindly supplied from SCG-Chemical Co., Ltd. The typical properties of the HDPE matrix used in this study reported from the manufacturer are summarized in Table 4.1.

Table 4.1 Properties of HDPE, EL-Lene H5814J

Properties	**Test Method**	**Value, Unit(SI)**
Melting Temperature	ASTM D2117	131^{o}C
Melt Flow Index	ASTM D1238@190/2.16	14 g/10min
Notched Izod Impact	ASTM D256	2 kJ/m^2
Tensile Strength at Yield	ASTM D638@50 mm/min	27.5 MPa
Elongation at Break	ASTM D638@50 mm/min	620%
Flexural Modulus	ASTM D790	1225 MPa
Heat Deflection Temperature	ASTM D648@0.455 MPa	75^{o}C

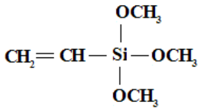
PTFE, Zonyl® MP 1300 fluoroadditive, is a free flowing white powder designed for using as an additive in other materials to impart low surface energy and other fluoro polymer attributions. It is available from DuPont® and it was employed as dispersed phase. According to the manufacturer data sheet provided, the powder has the particle size of 12 μm. Other properties of the powder are listed in Table 4.2.

Table 4.2 Properties of Poly(tetrafluoroethylene), Zonyl® MP 1300

Properties	**Test Method**	**Value, Unit**
Melting Temperature	ASTM D4894	325 ± 5^0C
Particle Size Distribution	Laser Microtrac	12 µm
Specific Surface Area	Nitrogen Adsorption	1.5 - 3.0 m^2/g
Average Bulk Density	ASTM D4894	0.425 kg/l

Low viscosity and water clear liquid vinyl trimethoxy silane (VTMS), commercialized as Silquest® A 171, was used as crosslink system in conjunction with peroxide through the moisture incubation or sauna treatment. The chemical structure and physical properties of the liquid silane is given in Table 4.3. The chemical was directly used without further dilution and purification.

Table 4.3 Properties of VTMS, Silquest® A171

Properties	Value, Unit
Chemical structure	 $CH_2=CH-\overset{OCH_3}{\underset{OCH_3}{Si}}-OCH_3$
Boiling point	122°C
Specific gravity, 25°C	0.967 g/ml

Low melting temperature, <50°C, solid dicumyl peroxide (DCP) flake was employed as free radical generator. It is a commercial grad and available throughout the rubber chemicals suppliers. The chemical formula of this peroxide is shown in Figure 4.2. Again, it was used without further purification. It has low melting point, slightly above 50°C. It is normally decomposed and generated quit stable free radical at the temperature above 120°C.

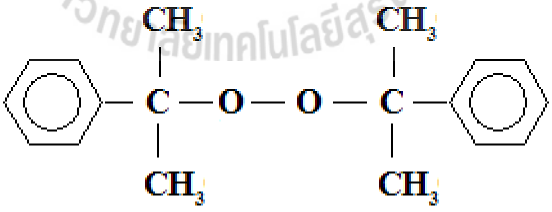


Figure 4.2 Chemical structure of dicumyl peroxide ($C_{18}H_{22}O_2$)

4.3.2 Melt mixing of HDPE /PTFE blends

The melt mixing procedures between HDPE and PTFE conducted in this research work is schematically shown in Figure 4.3. The PTFE powder was pretreated with silane/DCP as batch wise process in the internal mixer. The calculated amount, with respected to 100 g of PTFE powder, of 0.5 phr of DCP was priory dissolved in 1 phr of silane. The clear solution was promptly added into the PTFE powder in the mixing chamber equipped with the roller rotors. The surface treatment was performed at 100°C and rotors speed of 80 rpm for 5 minutes. The treated powder was stored in tightly sealed container for at least overnight.

HDPE was pre dried in the vacuum oven at 80°C for 2 hours. The solution of the desired amount of DCP and silane was completely dissolved. It was vigorously mixed with the dried HDPE pellet. Then, the pre calculate amount of the silane/DCP treated PTFE were added into the HDPE ingredient and completely well incorporated. The solid mixture was immediately fed via the single screw feeder into intermeshing co-rotating twin screw extruder having the screw diameter of 25 mm, L/D ratio of 20 and it is consisted of three quadrate kneader disk. The compounding processing was carried out at screw speed of 10 rpm at the constantly barrel temperature profile at 190°C for all 4 zones. The compounded strand was cooled down and cut into the pellet form.

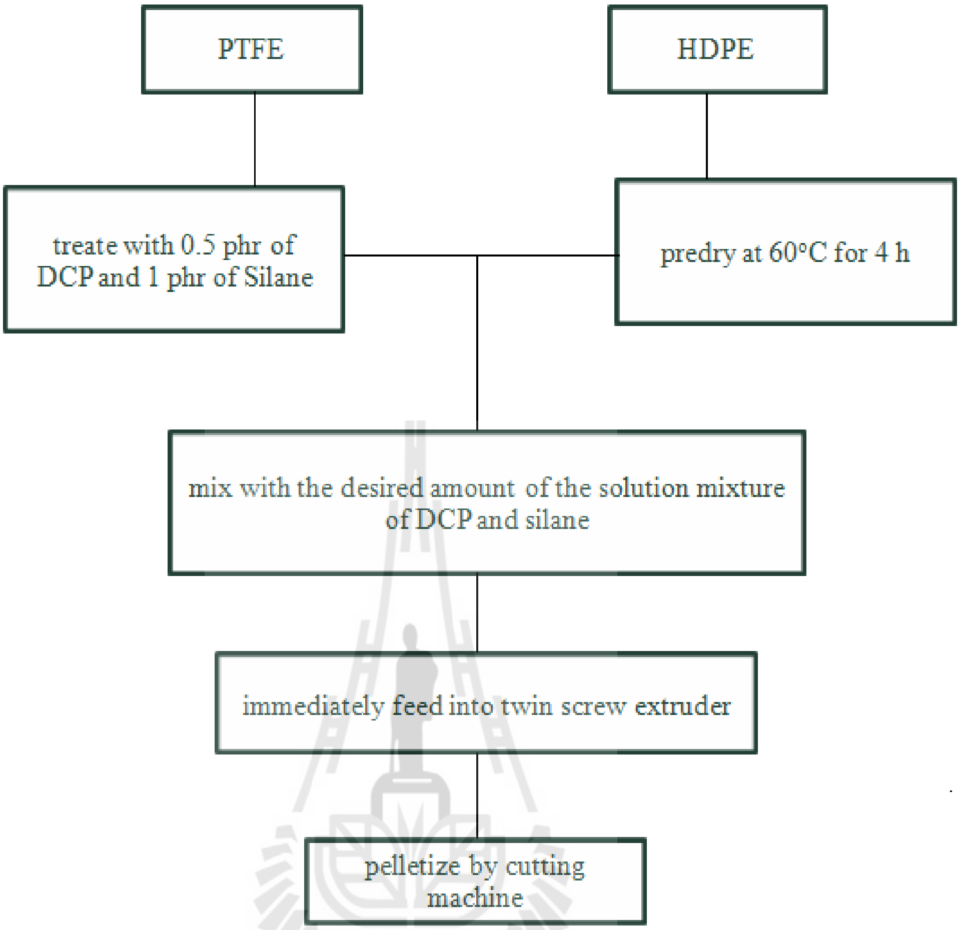


Figure 4.3 Schematic diagram of HDPE/PTFE blending procedure

4.3.3 Specimen Preparation

4.3.3.1 Injected Sample

The tensile, flexural and impact testing samples were prepared by injection molding using a reciprocating screw injection molding machine, CHUAN LIH FA T80. The temperatures profile for molding was 190, 200, 210 and 220°C from feed to nozzle, respectively. The family and artificially balanced two plate mold consisted of two dumb bells, type I and type IV, one rectangular bars for flexural and

HDT testing and one short rectangular bar for impact testing, was employed. The size and shape of the injected specimens were in accordance with ASTM regulations. The temperature of mold cooling water was carefully controlled at 30^{o}C. The injection pressure was electronically controlled at 80% of the maximum machine capacity. The injected samples were divided into 2 sets. The first one was allowed to anneal at room temperature overnight and they was categorized as “**original**” sample by definition of this study. The later was undergone post curing in the moisture saturated oven at 65^{o}C for more than 12 hours. The incubation temperature was close to the T_g of HDPE used allowing the moisture molecule to easily penetrate into the free space of the chain. Hence, the completion of the siloxane/moisture condensation could be accelerated and succeed. These treated specimens were classified as sauna cured or shortly as “**cured**” sample.

4.3.3.2 Sheet film sample

Thick film samples for the abrasion testing were obtained by hot press process. A few grams of the compound pellet were placed in between two PTFE/Glass woven sheets. The set up was transferred into the plat molds. The polymer was preheated at 200^{o}C for 10 min then slowly pressed at 110 MPa for 6 min. The pressed film was immediately removed and allowed to cool down at room temperature. The smooth film with the approximate thickness of 0.4 mm was obtained. The abrasion test specimen was scissor cut into the disk shaped with the diameter of 4.5 cm. The centered hole was punched. Accordingly, the sheet films were also divided into 2 set of test, original and sauna cured, respectively.

4.4 Properties Measurement

4.4.1 Rheological testing

The rheological property by mean of melt flow index (MFI) was conducted. The MFI of the HDPE/PTFE pellet was tested in accordance with ASTM D 1238 using the Kayeness melt flow indexer model 4004. The obtained pellet samples from vacuum dried in the oven at 80°C for at least 2 hours to eliminate the possible moisture residual. The polymer pellet was allowed to completely molten at 230°C for 240 seconds and it was driven through the capillary die (Ø 1 mm.) using piston load of 5.0 kg. Three cuts were performed at the cut times of 30 seconds. The extrudate was weighed and computed into the melt flow index in the standard unit of g/10min.

4.4.2 Performance testing

4.4.2.1 Impact strengths

Impact strengths of the HDPE/PTFE blends were tested in according with ASTM D 256 in the Izod mode. The injection molded specimen obtained with the dimension of 12x50x3 mm. was notched using the notching machine. The identical injected samples were tested without notching. Notched and unnotched impact strengths were conducted at room temperature using the impact pendulum with impact energy of 2.7 Joule for the notched specimen and 5.4 Joule for the unnotched sample, respectively. The impact values were reported as impact strength, kJ/m^2, that were calculated from impact energy required for completely breaking the sample over the cross section area at fractured area. At least five samples were tested for each polymer sample and the average value were obtained and recorded.

4.4.2.2 Flexural properties

Flexural properties by mean of the strength and modulus of the HDPE/PTFE sample were examined in accordance with ASTM D790. The injection molded sample with the dimension of 12x120x3.5 was used for the test. Instron universal testing machine, model 5565, with the load cell of 5 KN and three point bending test fixture with span length of 56 mm, approx. 16 times of the thickness, was employed. The crosshead speed of 50 mm/min was constantly controlled. The test specimen was placed plat wise to the bending load. The test was conducted at room temperature in normal atmospheric condition. The flexural strength and modulus were computerized using the following equation (4.1) and (4.2), respectively.

$$\textbf{Flexural Strength} = \frac{3PL}{2[bd]^2} \tag{4.1}$$

Where: P = load at a given point on the load-deflection curve (N)

L = support span (mm)

b = width of beam tested (mm)

d = depth of beam tested (mm)

and

$$\textbf{Flexural Modulus} =. \frac{L^3 m}{4(bd)^3} \tag{4.2}$$

Where: L = support span (mm)

b = width of beam tested (mm)

d = depth of beam tested (mm)

m = slope of the tangent to the initial straight line portion of the load-deflection curve (N/mm) of deflection.

4.4.2.3 Heat deflection temperature

Heat deflection temperature (HDT) of the HDPE/PTFE blend was conducted with the ASTM D 648. The sample was tested in the edgewise position, with the support span length of 100 mm. The simple beam with the standard load applied at its center to give maximum stress of 0.455 MPa or 66 psi was followed. The testing machine from Atlas, model HDV 1, was employed. The raising temperature at a uniform rate of 2 ± 0.2^{o}C/min was assigned. Liquid silicone oil was used as heating transfer media. The HDT value was reported in degree Celsius (^{o}C) as soon as the specimen had been deflected to 0.25 mm or 0.01 inch that monitored by the dial gauge. This temperature was recorded as the deflection temperature under the assigned standard flexural load of the test specimen. Three samples were examined and the average value was reported.

4.4.2.4 Tensile properties

Tensile properties of HDPE/PTFE blends were examined using an Instron universal testing machine, model 5565, with a load cell of 5 kN, crosshead speed of 50 mm/min and a gauge length of 80 mm. Tensile tests were performed according to ASTM D638. The dimension of the molded dumbbell shaped specimens, type I, with 12.7 mm in width at narrow section, 20 mm in overall width, 80 mm in gauge length, 165 mm in overall length and approx. 3.5 mm in thickness was used for performing the test. Five samples were tested in each blend sample. Calculated tensile strength (N/m^2 or Pa) was given by dividing the maximum load, in Newton force (N), by the average original cross sectional area in the gage length segment of the specimen in square meters (m^2). Calculated modulus of elasticity was performed by extending the initial linear portion of the load extension curve and dividing the difference in stress corresponding to any segment of section on this straight line by the corresponding difference in strain. Calculated percent elongation at break was computed by reading the extension at the fracture point and then dividing that extension by the original gage length and multiplies by 100.

4.4.3 Surface characteristic observation

4.4.3.1 Abrasion testing

Wear ability of the blend by mean of abrasion testing was investigated. The standard method namely ASTM D 4060 Abrasive Wear Testing, was followed. It is the measurement of the weight loss under the specified test conditions. In this study, specimens were abraded at 500 rounds of rotation under the constant load at 0.25 kg and abrader No. H-18. The weight loss of the sample was recorded as the below calculation. Three circular HDPE/PTFE blend sheet prepared by the procedure describe in section 4.3.4.2 was employed. Each of specimens was tested. The averaged the weight loss was presented.

$$\textbf{\%Weight loss} = \left[\frac{\text{Weight before test} - \text{Weight after test}}{\text{Weight Before test}}\right] \text{x } 100 \qquad (4.3)$$

4.4.3.2 Surface tension observation

The surface tension of the polymer film to the liquid is normally tested by surface angle measurement using the appropriate test liquid. At the presence time, such expensive equipment is not available in the research laboratory. Attempting to investigate the surface tension of HDPE/PTFE film was conducted by using the adaptive, or comparative, test method. The deionized water was used as the test liquid. The adopted method to evaluate the surface tension between the test liquid and the surface of the injected blends specimen or film were constructed. The micro pipette with the minimal volume capacity of 20 μl equipped with the micro tip adapter was used for applying the water drop. Drops of 1.0 μl of the deionized water through the micropipette were carefully placed onto the cloth dried surface of the blend sample. The diameter of the water drop (D_{sample}) was measured through the optical micro scope and analyzed digitally. The diameter of the water drop on the commercial PTFE/Glass woven sheet (D_{PTFE}) was obtained and used as referee values. It was assumed that it was the pure surface of PTFE film. Then, the ratio between the diameters of drop on the sample divided by the diameter of the drop on the standard PTFE sheet (D_{sample}/D_{PTFE}) was computed according to the equation 4.4. If the computed ratio is higher than 1.0, it means that the diameter of demonized water on the blend sample is larger than on the PTFE sheet. It indicates that the surface tension of the blend sample is higher than the surface tension of PTFE. Vice versa, if the ratio less than 1.0 is obtained, it reviews that the surface tension of the blend would be lower than the referee PTFE sheet.

$$D_{Sample}/D_{PTFE} = \frac{\text{Diameter of drop on sample}}{\text{Diameter of drop on the standard PTFE sheet}} \tag{4.4}$$

4.4.4 Morphological investigation

Morphology of the fractured surface of HDPE/PTFE obtained from the notched impact testing was examined using scanning electron microscope (SEM). The broken piece of specimen was cut in to small piece to fit the SEM sample holder. It was securely attached onto the sample holder. The samples were coated with layers of gold for 8 minutes by ionization before analysis. SEM photograph was taken using JOEL machine model JSM6400 at the typical accelerating voltage of 10 keV.

4.5 Results and discussions

According to the blending formula of HDPE/PTFE with increasing the vinyl silane contents shown Table 4.4, the silane was varied from 2.0 to 4.0 phr with respect to 100 g of HDPE. The PTFE and DCP were kept constant at 20 and 1 phr, respectively. The properties of the melt blended obtained with respect to the silane employed are being discussed.

Table 4.4 The blend formulation of HDPE/PTFE and the silane content

Sample	**HDPE** (g)	**PTFE**	**DCP**	**Silane**
		(g) (phr)	(g) (phr)	(g) (phr)
Blend(Sil2.0)	400	80(20)	4(1)	8(2.0)
Blend(Sil2.5)	400	80(20)	4(1)	10(2.5)
Blend(Sil3.0)	400	80(20)	4(1)	12(3.0)
Blend(Sil3.5)	400	80(20)	4(1)	14(3.5)
Blend(Sil4.0)	400	80(20)	4(1)	16(4.0)

4.5.1 Flow ability and silane contents

The Rheological properties by mean of MFI at 230/5.00 of the HDPE/PTFE blends with silane used are summarized in Table 4.5 and plotted in Figure 4.4. It is seen that the flow index do not obviously change with the silane addition. It suggests that the flow is independence of the silane addition. It would indicate that the network density does not increase with increasing only the coupling agent. Without the peroxide initiated, the formation of the grafted chains between vinyl group of silane and the polymer chains are not occurred. Hence, the melt viscosity of the blends would not be affected by the silane loading. Further supporting data will be verified this statement.

Table 4.5 Melt flow index of HDPE/PTFE blends with increasing silane

Sample	**MFI@200/5.00**
	(g/10min)
Blend(Sil2.0)	0.422±0.034
Blend(Sil2.5)	0.422±0.015
Blend(Sil3.0)	0.422±0.016
Blend(Sil3.5)	0.422±0.020
Blend(Sil4.0)	0.421±0.032

4.5.2 HDT and silane addition

The heat distortion temperatures measured at the standard load of 0.445 MPa of the HDPE/PTFE Blends are summarized in Table 4.6. The relationship between HDT and the silane used is also graphically shown in Figure 4.4. Again, it is seen that there is no obvious relationship between the silane consumption and the thermal property. The increasing in the HDT of the samples after undergoing the sauna treatment could be due to the increasing in the chain crystallinity of the polymer matrix during the prolong annealing. A marginally deviation of the test result could be from the self-condensation reaction of the hydrolyzed or partially hydrolyzed coupling agent of the liquid silane (Chotirat, Chaochanchaikul, and Sombatsompop, 2007). The main product of the self-condensation reaction formed flexible polysilanol molecules on the HDPE compound, and this could reduce the reactivity of the silane coupling agent to chemically interaction with the polymer matrix.

Table 4.6 Heat deflection temperature (HDT) of HDPE/PTFE blends

Sample	**HDT (^{0}C)**	
	Original	Cured
Blend(Sil2.0)	67.8±2.5	74.9±2.7
Blend(Sil2.5)	66.3±2.3	75.5±0.6
Blend(Sil3.0)	66.2±1.3	78.5±0.5
Blend(Sil3.5)	64.1±1.4	79.3±1.6
Blend(Sil4.0)	64.1±0.4	79.3±0.1

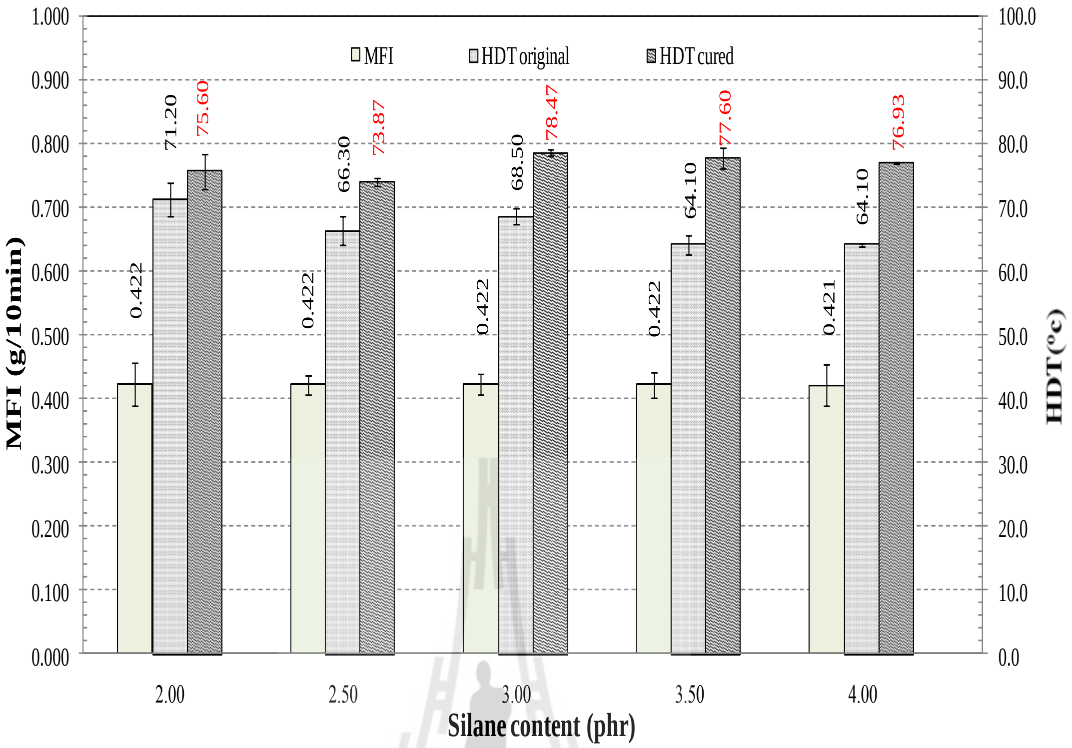


Figure 4.4 MFI and HDT of the HDPE/PTFE blends

4.5.2 Flexural properties and silane contents

Flexural properties of the HDPE/PTFE blends by mean of strength and modulus tested according to the standard method are given as numerical trend in Table 4.7. They are also graphical presented with respect to the silane used in Figure 4.5. It is observed that the strength of the blends is slowly decreased with increasing the silane contents. It is also observed that the strength is marginally higher after undergoing sauna curing process. Unexpectedly, the decreasing in the flexural strength with increasing the silane would be due to self-condensation reaction of the hydrolyzed or partially hydrolyzed coupling agent of the liquid silane. With the limit amount of DCP, the adding more of the vinyl coupling agent will not heighten the siloxane grafted sites. Hence, the crosslink density, derived from the intermolecular bridging, will not be further more occurred with increase the silane addition. The result would suggest that the ratio between silane and DCP at 2:1 by weight as the minimal used in this experiment is over the equilibrium ratio. In comparison between original and cured sample, it is seen that the flexural strength of cured sample is slightly higher than the original one. The assisting of the crystallinity improvement by annealing process at the high temperature and together with the crosslinking of the polymers chain, it would increase in the flexural strength of the blends as reviewed by the cured samples.

For the flexural modulus of the HDPE/PTFE blends, it is seen that the modulus is trendily decrease with adding more of silane in the blends for both original and sauna cured samples. It also seen that the modulus of cured is fractionally higher than the original one. The same hypothesis, the self-condensation reaction of the liquid silane reduced the reactivity of the silane coupling agent to chemically interaction with the polymer matrix and formed flexible polysilanol molecules on the polymer blend.

According to the flexural testing outcome, it could suggest that the increasing in the silane/DCP ratio on the HDPE/PTFE blending does not increase the crosslink density of the polymer chain. It might be the fact that the ratios used are beyond the equilibrium concentration as the DCP act as the limiting agent for the crosslink reaction through the siloxane/moisture condensation. Further increase the liquid silane fraction would has the self-condensation reaction of the liquid silane resulting the material to behavior like elastomeric in nature.

Table 4.7 Flexural properties of HDPE/PTFE blend with increasing silane addition

Sample	**Flexural strength (MPa)**		**Flexural modulus (GPa)**	
	Original	Cured	Original	Cured
Blend(Sil2.0)	40.30±1.68	40.44±1.77	2.132±0.160	2.220±0.098
Blend(Sil2.5)	38.24±0.53	40.14±1.17	1.974±0.117	2.198±0.072
Blend(Sil3.0)	37.85±0.97	38.88±1.32	1.944±0.077	2.102±0.065
Blend(Sil3.5)	36.95±1.34	38.66±2.35	1.954±0.178	2.094±0.101
Blend(Sil4.0)	36.68±0.99	38.16±1.30	1.906±0.104	2.034±0.074

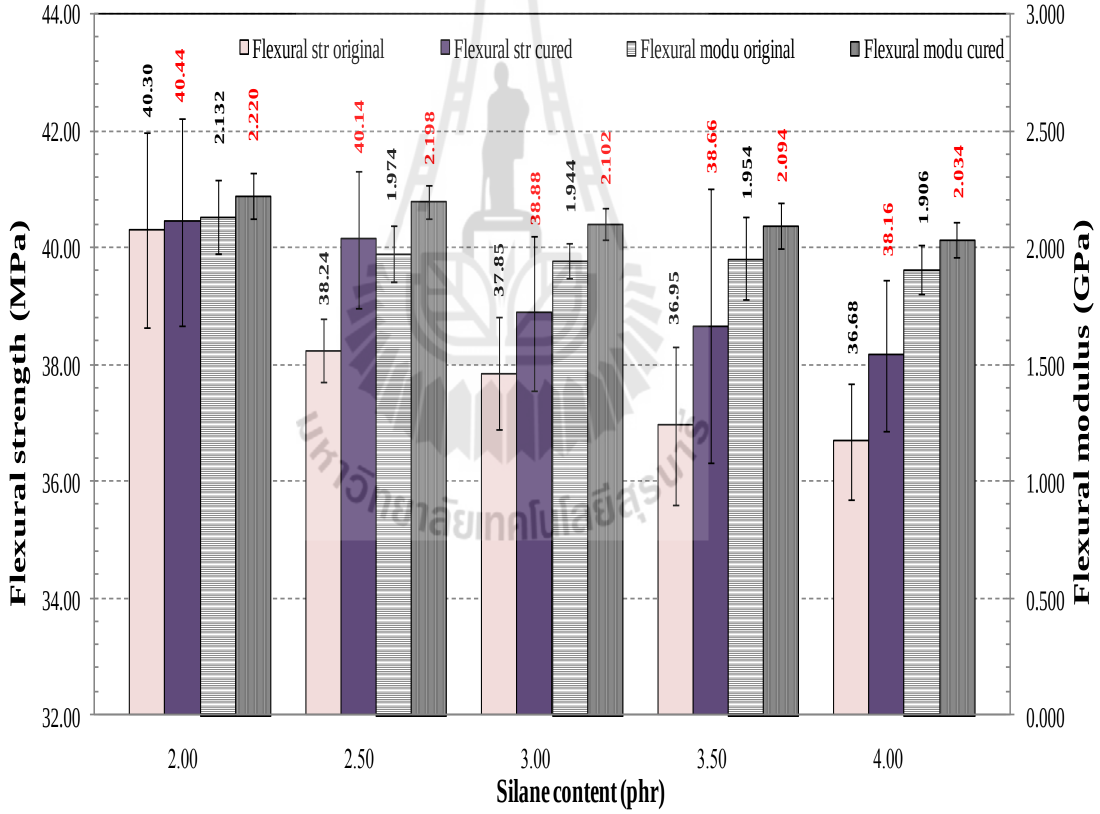


Figure 4.5 Flexural properties of HDPE/PTFE blends

4.5.3 Tensile properties of HDPE/PTFE blends with silane contents

Tensile properties, strength, modulus and % strain at break, of the HDPE/PTFE blends with respect to the silane contents are shown in Table 4.8. Within the standard deviation, it is seen that the strength of the original samples do not depend on the silane concentration. But for the test performed on the sauna cured specimen, the strength is tiny decreased with increasing the silane addition. The similar trend is also found the tensile modulus and % strain at break. In normal fashion, the increasing in the strength and modulus but decreasing in the % strain at break would be observed for the polymeric material with increasing the crosslink density. From the result obtained from this research study it is indicated that the network chains are not increased with increasing the silane concentration in the blend ingredients. The small changing in the tensile properties would be due to the two effects; the self-condensation reaction of the liquid silane and crystallinity via the prolong sauna annealing, as explain in the previous flexural section. More soften material would be obtained when more excess silane is added.

The tensile values are again strengthen that there is no further crosslink density increase when the ratio between silane and DCP is increased more than 2:1 by weight. Because of, the amount of peroxide is limited. Therefore, the number of siloxane grafted site on the polymer chain cannot be amplified. Consequently, the number of the intermolecular bridging through the silane/moisture incubation is not achieved.

Table 4.8 Tensile properties of HDPE/PTFE blends with increasing silane addition

Sample	Tensile strength(MPa)		Tensile modulus (GPa)		Elongation at break (%)	
	Original	Cured	Original	Cured	Original	Cured
Blend(Sil2.0)	22.11±0.47	23.36±0.45	0.778±0.008	0.816±0.050	56.77±0.08	59.55±2.01
Blend(Sil2.5)	22.52±0.32	23.14±0.41	0.792±0.063	0.760±0.060	55.74±2.35	61.41±6.55
Blend(Sil3.0)	22.62±0.21	22.86±0.65	0.764±0.105	0.826±0.055	54.34±3.98	51.00±8.10
Blend(Sil3.5)	22.66±0.11	22.40±0.71	0.790±0.053	0.734±0.131	54.34±1.83	53.48±5.60
Blend(Sil4.0)	22.66±0.26	21.60±0.42	0.762±0.073	0.672±0.051	54.37±3.98	55.77±4.80

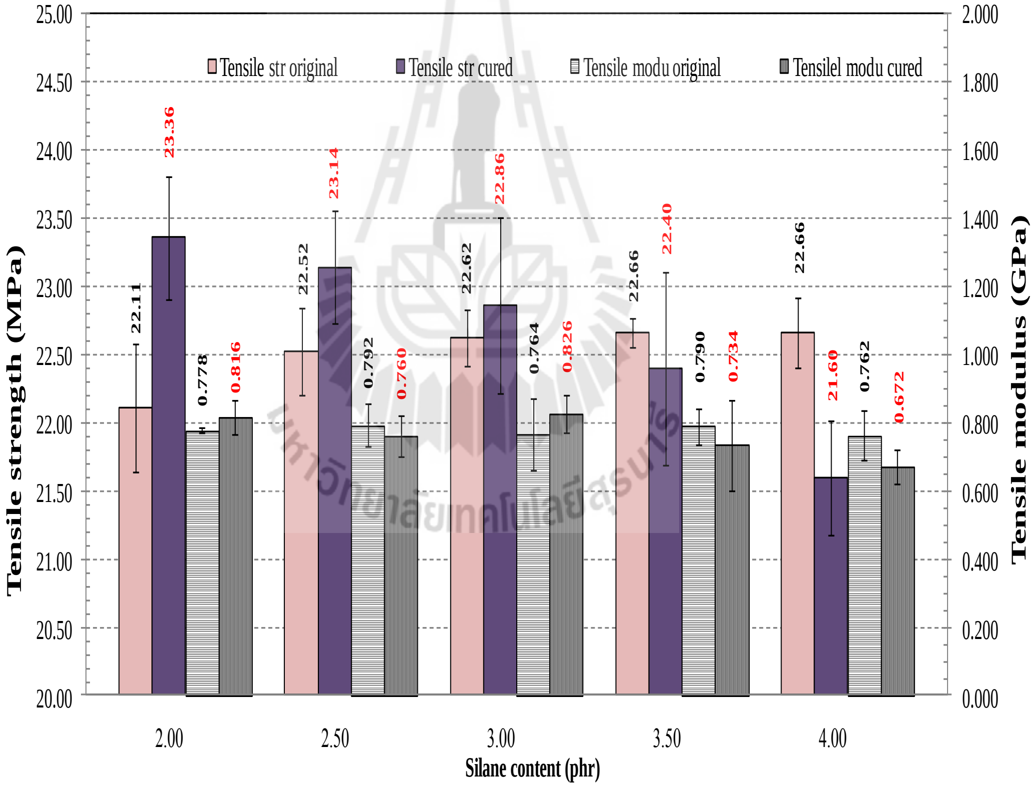


Figure 4.6 Tensile strength and modulus of HDPE/PTFE blends

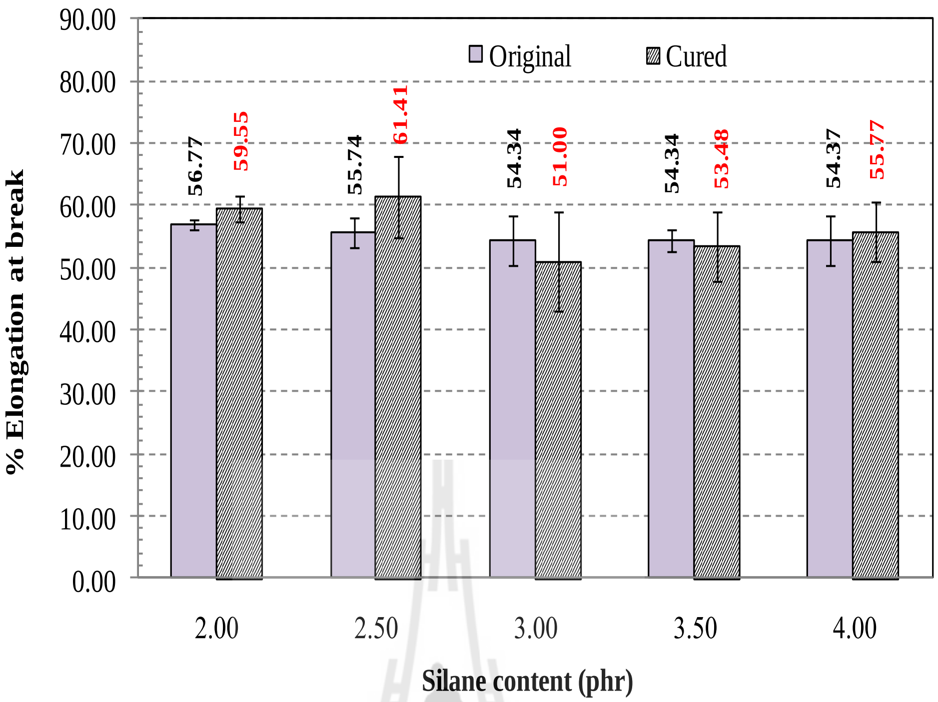


Figure 4.7 Elongation at break of HDPE/PTFE blends

4.5.4 Impact strength and silane contents

The fracture toughness of HDPE/PTFE blends was obtained as the notched and unnotched impact strengths. The notched test result conducted on the original and cured samples are summarized in Table 4.9 and they are plotted against the silane concentration shown in Figure 4.8. For the unnotched mode of text the numeric test figures cannot be reported because all of the samples were not broken by using the 5.4 kJ impact pendulum. From the summarization, it is seen that the strength is slowly increased with increasing the silane use for both types of specimen. It is also visual that at the given silane content the test value is marginally higher after it was undergone the moisture treatment. The tendency in positive changing on the strength with utilizing the silane would be due to the self-condensation reaction of the liquid silane coupling agent as discussed in the previous section. The more of the formed flexible polysilanol molecules in the blend ingredient the more elastic like material would be. Therefore, the blends would become more elastomeric like in nature, higher in toughness.

Again, according to the impact investigation, the results indicate that there are no evidences for increasing the chain network density by adding more of silane coupling agent. But, the excess silane would cause the self-condensation reaction of the liquid silane to the final blends. Consequently, more flexible, or elastomeric like material, would be resolved.

Table 4.9 Impact strengths of HDPE/PTFE blends with increasing silane addition

Sample	**Notched (KJ/m^2)**		**Unnotched (KJ/m^2)**	
	Original	Cured	Original	Cured
Blend(Sil2.0)	4.01±0.25	4.18±0.18	NB	NB
Blend(Sil2.5)	4.02±0.21	4.49±0.21	NB	NB
Blend(Sil3.0)	4.35±0.13	4.77±0.19	NB	NB
Blend(Sil3.5)	4.43±0.14	4.99±0.25	NB	NB
Blend(Sil4.0)	4.46±0.11	5.04±0.07	NB	NB

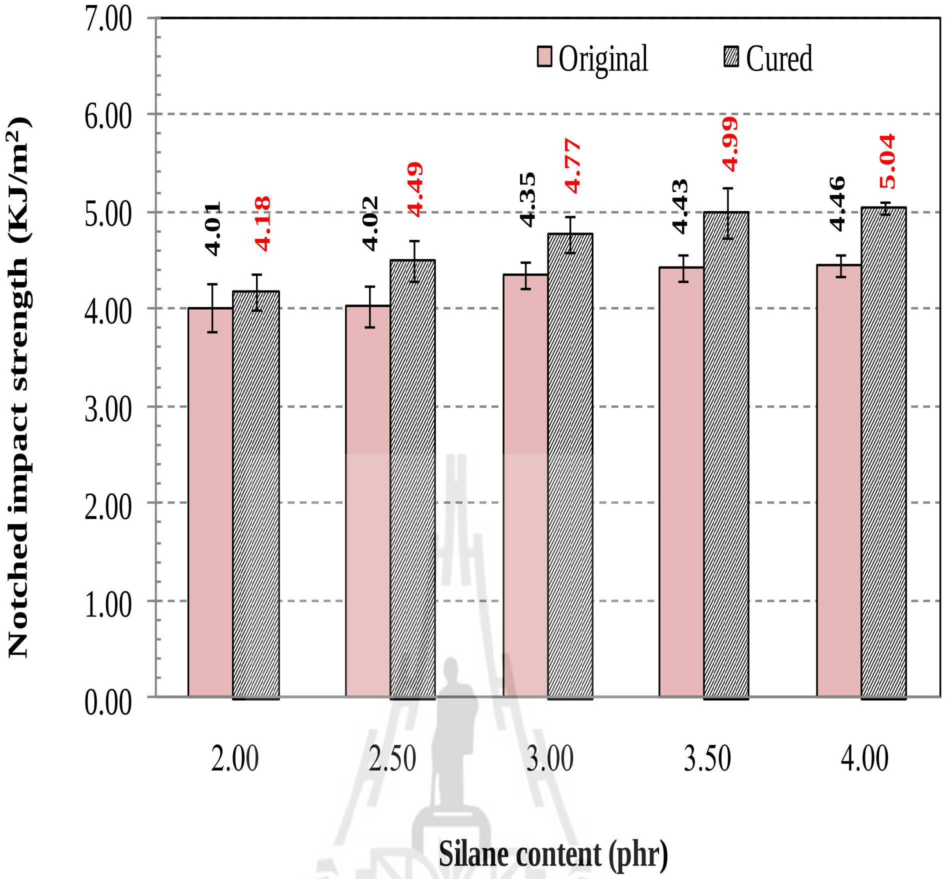


Figure 4.8 Notched impact strength of HDPE/PTFE blends

4.5.5 Water drop ratio investigation

Surface tension of the blends were observed by mean of water drop diameter ratio on the film of HDPE/PTFE blends sample and the referee material, PTFE/glass sheet (D_{sample}/D_{PTFE}). The calculation outcome is given in Table 4.10 and it is presented as the graphical relationship with the silane in Figure 4.9. Taken the standard deviation for the granted within this study, it would say that the surface tensions of the film samples are not depended on the amount of silane added. The ratios are almost constant for all obtained samples. Nevertheless, in comparison between original and cured conditions it is seen that the ratio is lower after the sauna incubation. It is indicated that low surface tension is obtained. It would result from the neutralization of the polar siloxane group on the surface of the film into the non polar element through the moisture reaction. As the result, the surface would become less tension to the water drop. But this effect would be minimal because there is not so many silane boomed on the surface of the film blends.

Table 4.10 Water drop diameter ratio of HDPE/PTFE blends with increasing silane addition

Sample	**D_{sample} /D $_{PTFE}$**	
	Original	Cured
Blend(Sil2.0)	1.03±0.09	1.01±0.08
Blend(Sil2.5)	1.03±0.11	1.01±0.02
Blend(Sil3.0)	1.04±0.05	1.00±0.12
Blend(Sil3.5)	1.04±0.05	0.98±0.24
Blend(Sil4.0)	1.04±0.04	0.96±0.07

4.5.6 Wear resistance of the blends and silane contents

The wear resistance, tested as the % weight loss under constant load, of the HDPE/PTFE blends is summarized in Table 4.11 for both original and cured samples, respectively. Evidently, the test values of both samples are decreased with increasing the silane loading. The superior in the wear of the samples is found after it was treated in the sauna oven at 65°C for more than 12 hours. This result is agreed with the increasing in toughness properties of the blends by adding more of silane as discussed earlier. Normally, the material with high flexible or elastomeric like with lower T_g would have higher wear resistance than the rigid or brittle ones. Therefore, the blends with higher in the excess silane, more dilution effect, and dominated by the flexible material in nature, would have the higher in wear resistance, lower in the % weight loss. Also, the competency in the wear after treating in the sauna oven could be due to the two folds explanation; (*i*) reinforcement effect of the increasing of more rigid crystalline segment formed during the prolong annealing and (*ii*) superior in the internal interface adhesion between flexible amorphous and rigid crystalline pools by the silane primer. Accordingly, excellence wear property might be occurred.

Table 4.11 Abrasive resistances of HDPE/PTFE blends with increasing silane addition

Sample	**Weight loss (%)**	
	Original	Cured
Blend(Sil2.0)	0.56±0.02	0.25±0.03
Blend(Sil2.5)	0.48±0.02	0.25±0.02
Blend(Sil3.0)	0.48±0.05	0.23±0.05
Blend(Sil3.5)	0.41±0.06	0.18±0.03
Blend(Sil4.0)	0.40±0.08	0.11±0.03

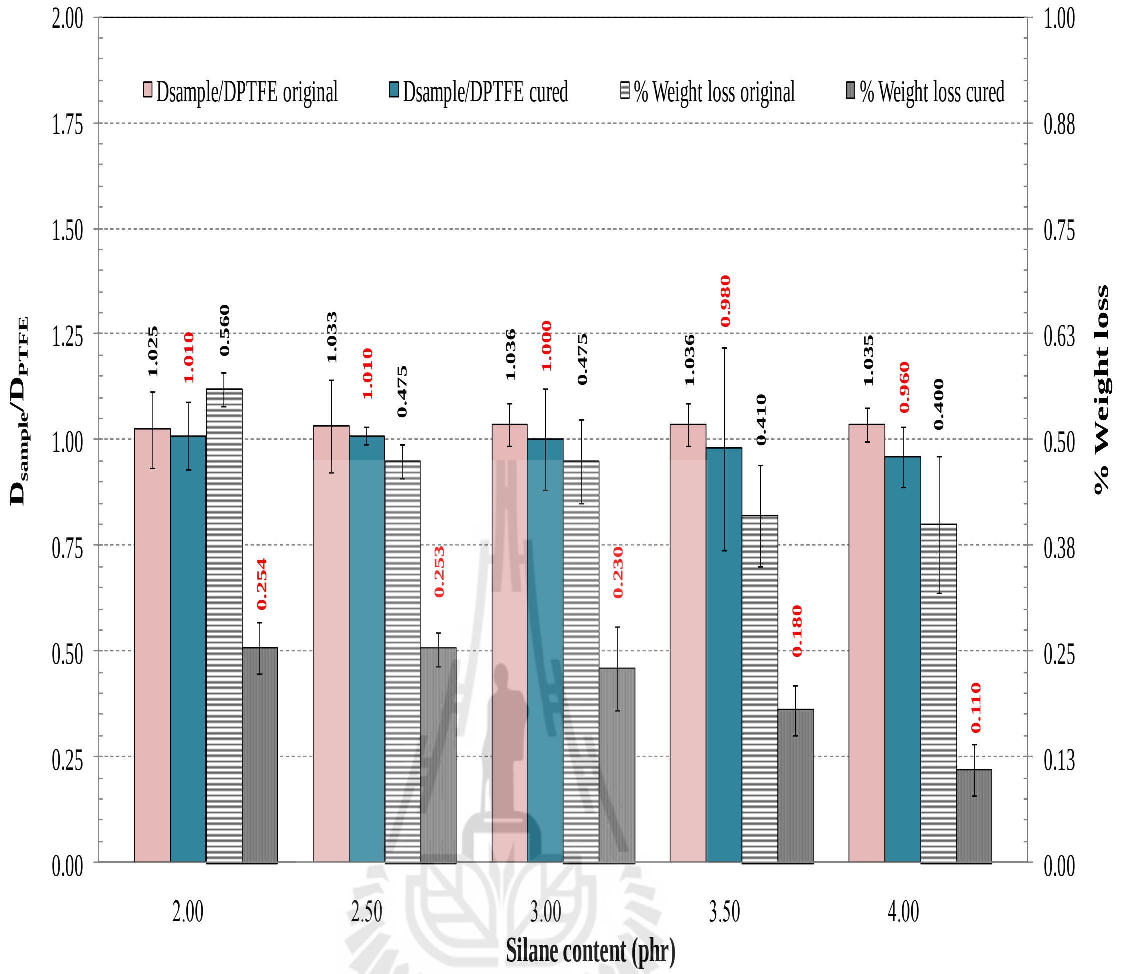
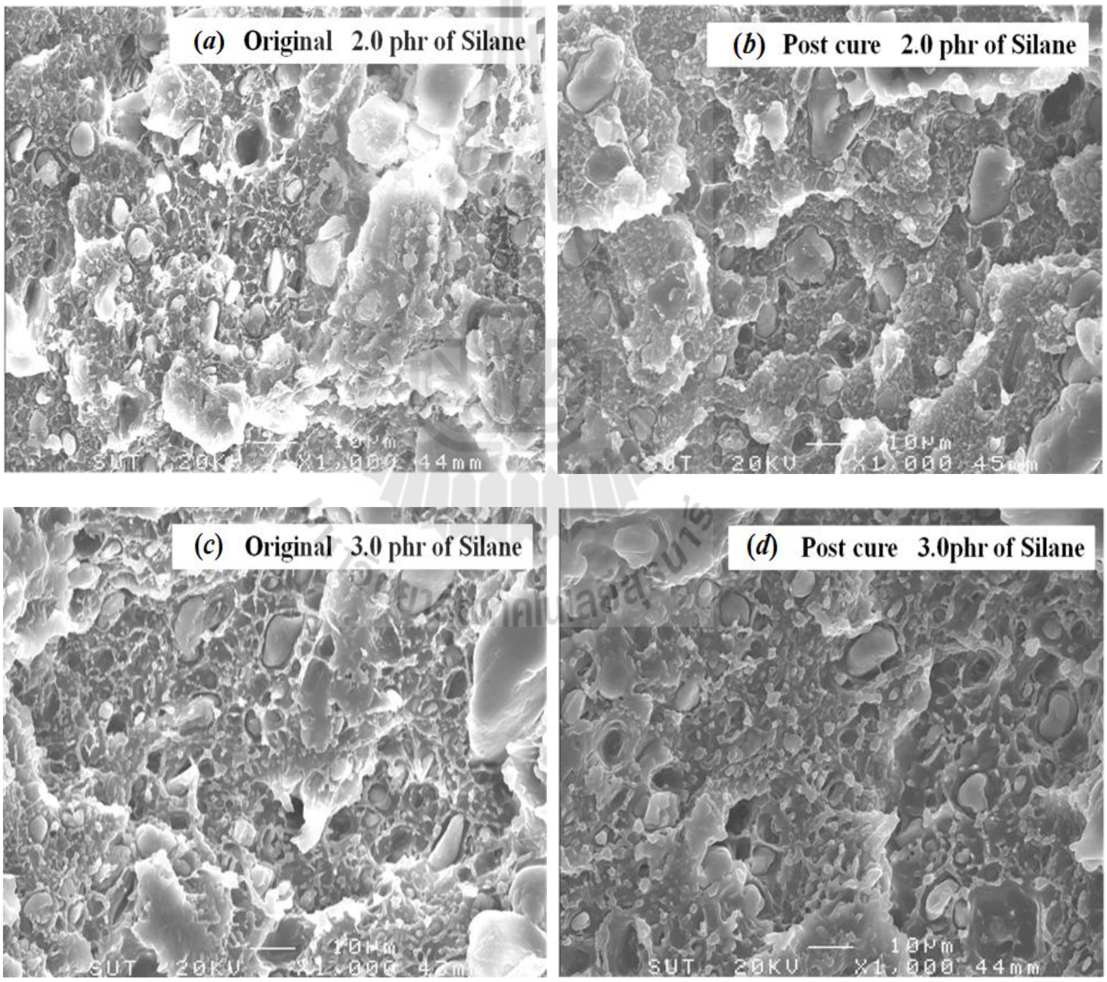


Figure 4.9 Surface properties of HDPE/PTFE blends

4.5.7 SEM visualization

SEM micrographs at X1000 of HDPE/PTFE blends with 2.0, 3.0 and 4.0 phr of silane are displayed in Figure 4.10 **(*a*)** and 4.10 **(*f*)** for original and cured, respectively. It is obviously seen that the PTFE particle is dispersed on the HDPE matrix. The PTFE pull out is the major crake phenomenon. According to the morphological observation, increasing in the silane contents does not manifest any vast improvement of the adhesion between the particle and the matrix. This indication could be used to explain why the tensile and flexural properties of the HDPE/PTFE blends do not superior by increasing the silane content as described earlier. Closer investigation of the fractured surface, it is seen that the web like traces at the matrix, HDPE, is more obvious after sample undergo sauna incubation. Also, the numbers of webs do seemingly and directly depend on the amount of silane used. The web like traces could be resulted from the silane/moisture crosslink reaction. The network density would increase with increasing the silane addition.



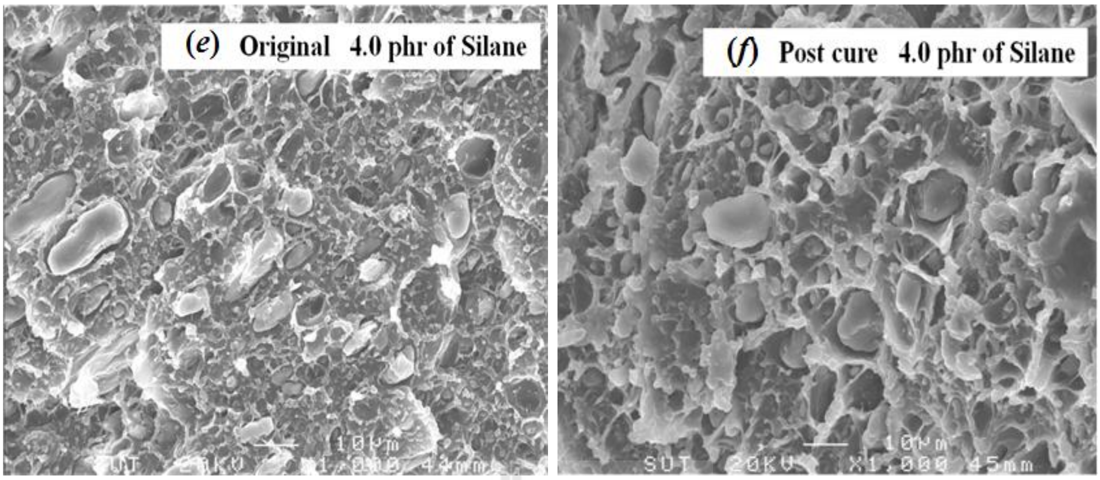


Figure 4.10 SEM micrographs of HDPE/PTFE blend with different concentrations of silane; (*a*) 2.0 original (*b*) 2.0 cured (*c*) 3.0 original (*d*) 3.0 cured (*e*) 4.0 original and (*f*) 4.0 cured, respectively.

4.5.8 Treatment temperature of PTFE powder by DCP/silane and the properties of the treated PTFE/HDPE blends

The degradation temperature and the possible reaction between the generated free radical on the surface of PTFE powder would likely to depend on the temperature. It was scientifically interested for this research work to explore the effect of the temperature on the surface treatment of the free radical initiated PTFE particle by DCP/silane in the internal mixer. In this study, the PTFE powder was treated with 0.5 phr of DCP and 1.0 phr of silane at the chamber temperature of 100 ^{o}C, 120 ^{o}C 130 ^{o}C and 150^{o}C with the constants rotors speed at 80 rpm for 5 mins and they were used for blending with HDPE. Original PTFE powder with no chemical treatment was blended with HDPE and used as the referee material. The HDPE/PTFE blending formulae were consisted of 20 phr of treated PTFE, 1.0 phr of DCP and 4.0 phr of silane. The standard tests were employed to examine the effect of the treatment temperature and the test results of the HDPE/PTFE blends are being discussed in this section.

4.5.8.1 MFI of treated PTFE/HDPE Blends

The melt flow index of the HDPE/PTFE blends at 230/5.0 obtained from DCP treated PTFE powder at the treatment temperature of 100, 120, 130, 150°C and without treatment is presented in Table 4.12, respectively. It is also graphically illustrated with respect to the temperature in Figure 4.11. Generally observation, it is noticed that the MFI of the blend does not depend on the decomposition temperature of DCP. It is well known that the PTFE is one of the most chemically inert polymers. Taken the MFI result as the scientifically respond, it could state that the temperature ranging from 100 – 150°C could not successfully induce the reaction between PTFE and free radical generated from the DCP decomposition. Consequently, the amount of silane grafted onto the PTFE would not be changed with the treating temperature. No change in the grafted side means no increasing in the crosslink density and/or chains extension via the in-situ blending with HDPE. Therefore, the melt viscosity of the derived blend would be constant.

Table 4.12 Treatment temperature of PTFE and the MFI of HDPE/PTFE blends

Treated Temp. (°C)	**MFI@230/5.00** (g/10min)
untreated	0.431±0.012
100	0.421±0.032
120	0.421±0.005
130	0.422±0.033
150	0.422±0.021

4.5.8.2 HDT of HDPE/PTFE blends

The HDT of HDPE/PTFE blend at 0.445 MPa of the HDPE/PTFE blends prepared from PTFE powder treated at various temperatures is summarized in Table 4.13 and it is also graphically given in Figure 4.11. Again, it is seen that the HDT of both before and after sauna curing of HDPE/PTFE blends are more or less unchanged with the treatment temperature of PTFE powder before blending with HDPE. However, when compare with the PTFE blend without DCP treatment, it is quite noticed that the distortion temperature of the blend with DCP treatment are higher than the one without treatment for both samples conditioned. The interfacial surface enhancement via the DCP treatment of PTFE could be considered. This piece of evidence will be further illuminated later on this section. Carefully discussion, the result also reveals that the sauna curing causes the elevating the heat distortion of the blend. The improvement in the crystallinity of HDPE would be the major effect for the rising of HDT.

Similar to the MFI outcome, it could review again that the increasing of the decomposition temperature of DCP during the PTFE surface treatment by free radical in the internal mixing chamber does not has the significant effect on the HDT of the blend material. The HDT of the blends do not depend on the treatment temperature. Hence, there is no changing in the silane grafting onto the PTFE surface. As the result, there is no increasing in the chain extension neither by grafted nor crosslink during the blending with HDPE. Normally, if there is no chain extension, it would be no increasing in the HDT.

Table 4.13 Treating condition and HDT of HDPE/PTFE blends

Treated Temp. (^{o}C)	**HDT (^{0}C)**	
	Original	Cured
untreated	62.2±0.1	73.3±0.7
100	64.1±0.4	76.3±0.1
120	64.1±0.1	76.9±0.1
130	64.0±0.4	77.0±0.2
150	64.1±0.1	77.0±0.4

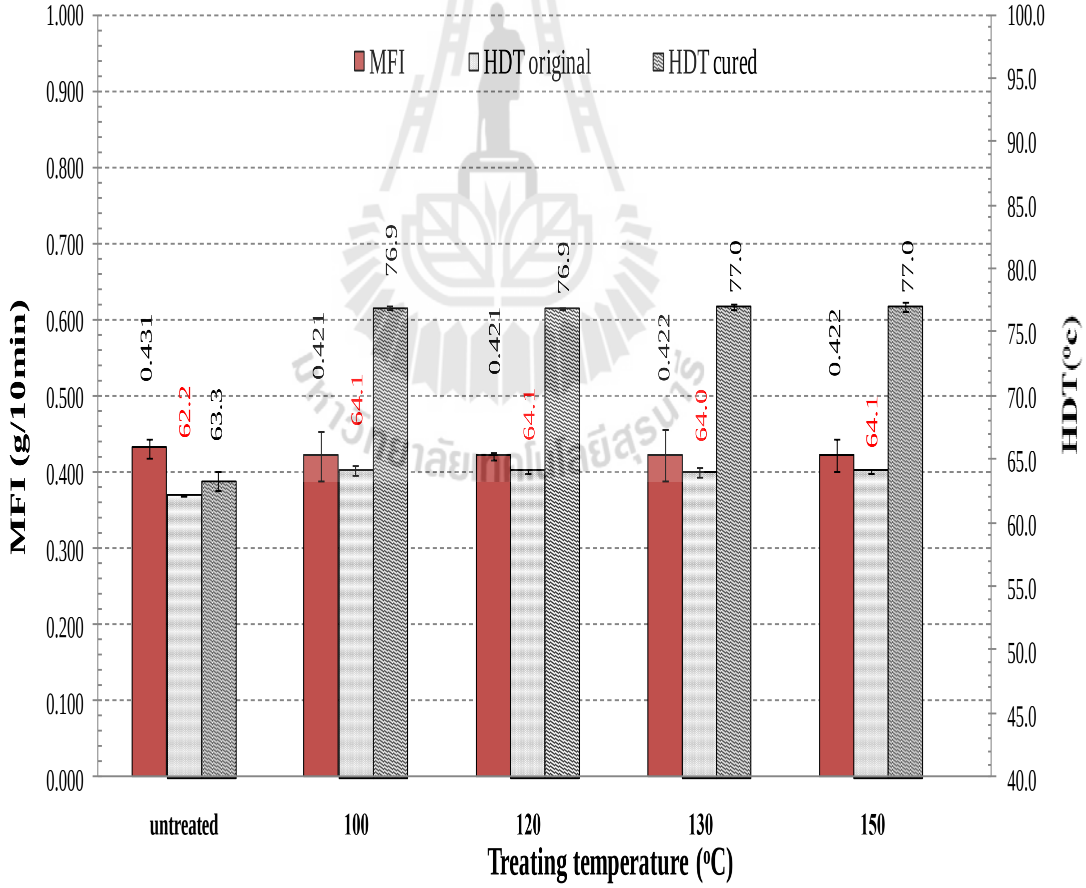


Figure 4.11 MFI and HDT of the HDPE/PTFE blends

4.5.8.3 Flexural properties of HDPE/PTFE blends

The flexural properties, by mean of strength and modulus, of HDPE/PTFE blends using treated PTFE at various temperatures are reported in Table 4.14. It is also plotted with respect to the temperatures in Figure 4.12. It is observed that there is no difference in test results, both strength and modulus, with respect to the treatment temperature of PTFE particle by using DCP, of HDPE/PTFE blends However within the standard deviation obtained, in comparison between untreated and treated PTFE, it is evidenced that the flexural properties of untreated HDPE/PTFE is slightly lower than the treated one. The observation is quite obvious when the sample was undergone sauna incubation. This could be resulted from the improvement of the interfacial tension of PTFE during the free radical reaction. Therefore, good interfacial adhesion between PTFE and HDPE during melt blending would be resolved. Further enhancement would be successfully occurred during the prolong sauna incubation. The morphological investigation will be used to strengthen this statement later on this section.

Generally, the flexural strength and modulus of the HDPE/PTFE blends do not change when the PTFE powder was priory treated with DCP at the temperature at 100, 120, 130, 150^{o}C, respectively. At this point of discussion, it could strengthen the previous statement that the free radical generated from DCP decomposition cannot react or chemically modified, at the temperature below 150^{o}C, the surface of PTFE. Accordingly, the physically properties of the blend between treated PTFE and HDPE cannot be alternated by the treatment temperatures.

Table 4.14 Flexural properties of HDPE/PTFE blends

Treating Temp. (°C)	**Flexural strength(MPa)**		**Fluxuralmodulus(GPa)**	
	Original	Cured	Original	Cured
untreated	33.34±0.58	33.18±0.76	1.770±0.019	1.860±0.033
100	33.68±0.99	36.16±1.30	1.810±0.100	1.945±0.070
120	33.91±1.25	36.01±0.81	1.804±0.152	1.922±0.086
130	34.16±0.95	35.88±2.43	1.792±0.070	1.896±0.187
150	34.31±0.70	36.14±2.17	1.804±0.057	1.932±0.188

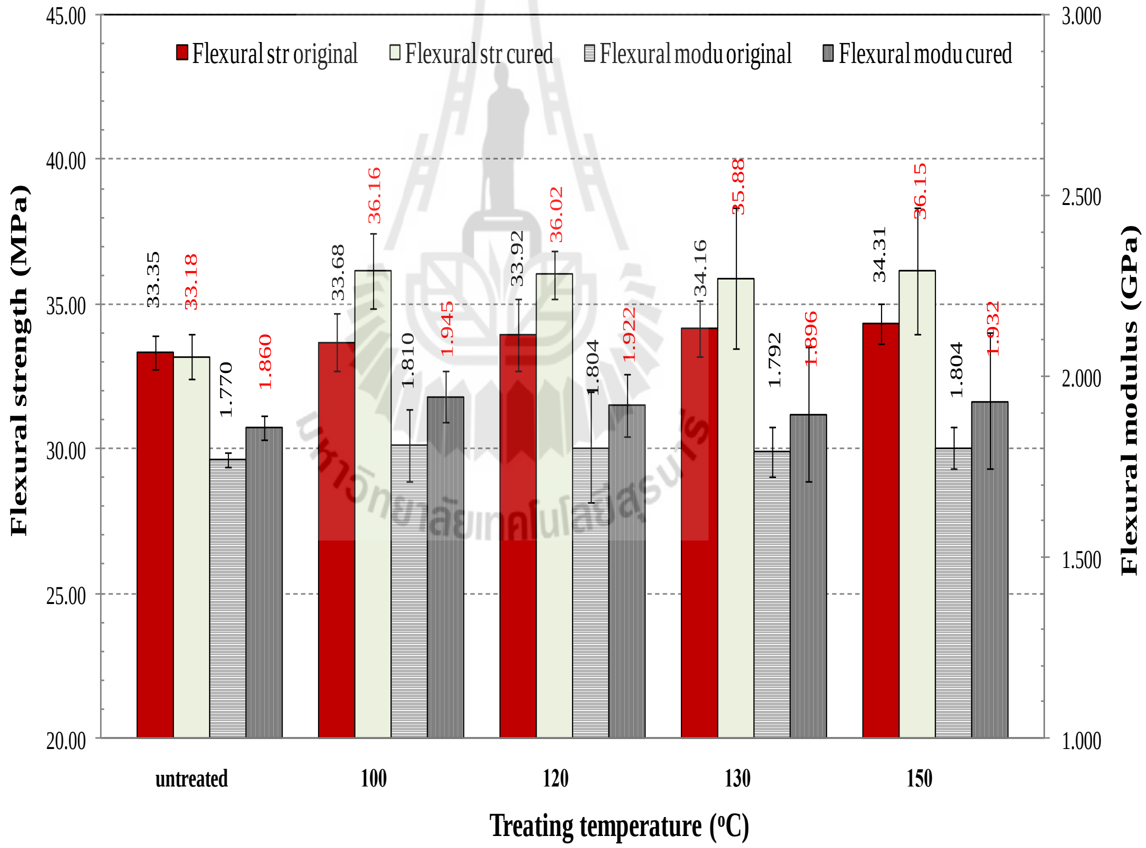


Figure 4.12 Flexural properties HDPE/PTFE blends

4.5.8.4 Tensile properties of HDPE/PTFE blends

Tensile properties; strength, modulus and % elongation at break, of the HDPE blends with treated and untreated PTFE obtained at strain rate of 50 mm/min are shown in Table 4.15. Mean while, Figure 4.13 is the plot between the strength and modulus with the various treating conditions. According to the test values found and within the standard deviation obtained, it is seen that there is no significant different, for both original and sauna cured, in the strength of the blends derived from treated and untreated PTFE and also the surface treatment temperature. However, considering the modulus of the HDPE/PTFE blend, both with and without sauna treatment, it is noticed that the test values of the untreated sample are slightly higher than the treated specimen. Meanwhile, the temperature seems to have no effect on the modulus of the blends.

Figure 4.14 illustrates the relationship between % elongations at break and the temperature applied for surface treatment of PTFE. Generally, the test result reveals the similar trend that was observed in the tensile strength and modulus. The % elongation of the blend derived from the untreated PTFE is noticeably higher than the treated ones. There is no obvious distinctive value regarding to the remediation temperatures.

Taken the tensile properties as the indicator for discussion the effect of surface conditioning of PTFE by using the temperature, the similar trends as found earlier are repeated. The surface treatment of PTFE by using free radical decomposed from DCP, regardless to the temperature, has the effect on the interfacial adhesion between HDPE and PTFE in the presence of DCP/silane crosslink agent. The tensile testing indicated that slightly lower in strength, modulus and % elongation are due to the treatment of PTFE before blending with HDPE. Lower in the tensile characteristics mean lower in the toughness under the tension force, or more brittle material. Interfacial adhesion between flexible HDPE with rigid PTFE particles would retard the HDPE deformation. Consequently, the blend would be strained less than the material having no surface adhesion. It means that the blend behave less ductile under the tension force.

Table 4.15 Treating condition and Tensile properties of HDPE/PTFE blends

Treating Temp. (°C)	**Tensile strength(MPa)**		**Tensile modulus (GPa)**		**Elongation at break (%)**	
	Original	Cured	Original	Cured	Original	Cured
untreated	19.71±0.30	21.30±0.51	0.622±0.022	0.682±0.029	63.13±4.21	58.51±7.02
100	19.66±0.26	21.60±0.42	0.560±0.070	0.670±0.050	54.37±3.89	55.77±4.80
120	19.45±0.95	21.20±0.40	0.524±0.049	0.608±0.036	58.83±3.92	55.67±9.96
130	19.91±0.16	21.44±0.28	0.568±0.036	0.570±0.010	51.59±7.07	48.68±3.33
150	19.86±0.34	21.35±0.22	0.586±0.052	0.588±0.015	58.80±6.96	49.39±9.65

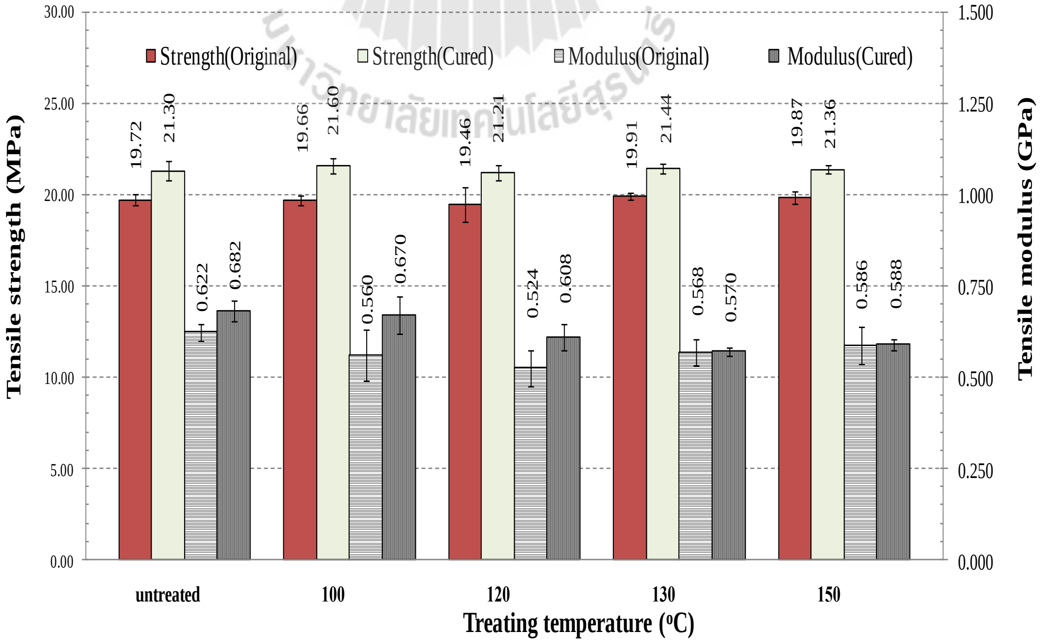


Figure 4.13 Effect of treating temperature on tensile properties HDPE/PTFE blends

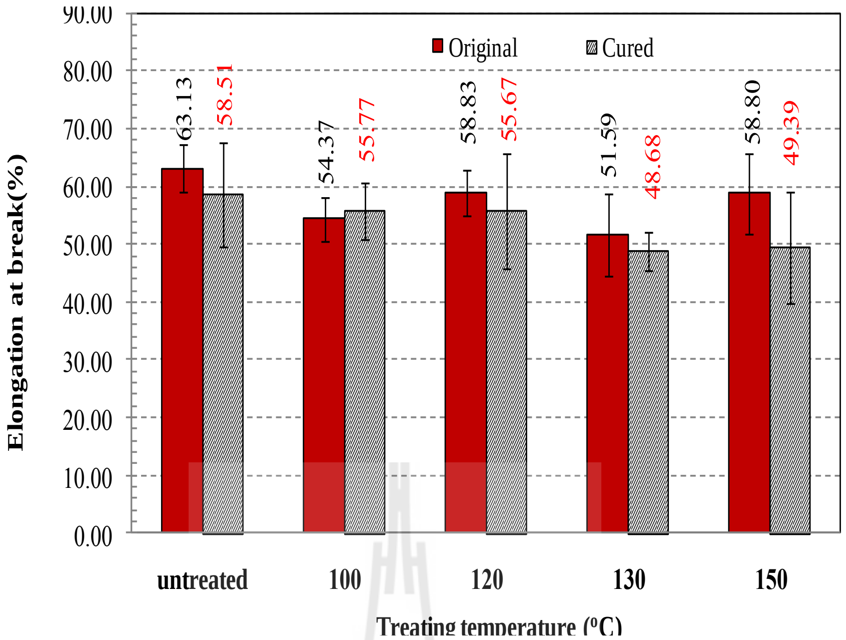


Figure 4.14 Effect of surface treatment temperature on elongation at break of HDPE/PTFE blends

4.5.8.5 Analysis of impact strengths

The pendulum impact characterization is direct method to verify the toughness of the polymeric materials. The effect of PTFE surface conditioning on the fracture toughness by mean of impact measurement of HDPE/PTFE blend, for both original and cured samples, are summarized in Table 4.16. They are presented as the graphical relationship with the treatment temperature in Figure 4.15. By using the impact pendulum at 5.4 J for the unnotched samples, it was not enough sufficient energy to fail the sample. Therefore, no specific impact strength is reported for the unnotched specimen.

For the notched impact strength test values, it is also observed that the impact strength of the HDPE/PTFE blends is likely to increase with increasing treatment temperature of PTFE for both original and cured specimen, respectively. However, the magnitude of change is tiny. It is an ambiguous to conclude that the temperature had the positive effect on the impact strength of the blends. Meanwhile, it quite obvious when compare the strengths between the untreated PTFE and treated PTFE. The formal blend sample shows the lower toughness than the treated one. The result, again, reveals that the surface improvement of treated PTFE is gained and hence show the impact toughness of the polymer blends is superior. Further investigation also exposes that the induction of silane/moisture reaction via the sauna incubation shows the positive effect on the impact strength of the HDPE/PTFE blends. The reaction would generate the stronger bonding between HDPE matrix and the surface of PTFE particle. Better interfacial adhesion between continuous phase and particle greater in the toughness under the impact force.

Table 4.16 DCP surface treatment temperature of PTFE and impact strengths of HDPE/PTFE blends

Treating	**Notched (KJ/m^2)**		**Unnotched (KJ/m^2)**	
Temp. (^{o}C)	Original	Cured	Original	Cured
untreated	5.41±0.80	7.09±0.07	NB	NB
100	7.46±0.11	7.64±0.07	NB	NB
120	7.49±0.80	7.70±0.15	NB	NB
130	7.74±0.91	7.85±0.63	NB	NB
150	7.75±0.76	7.84±0.63	NB	NB

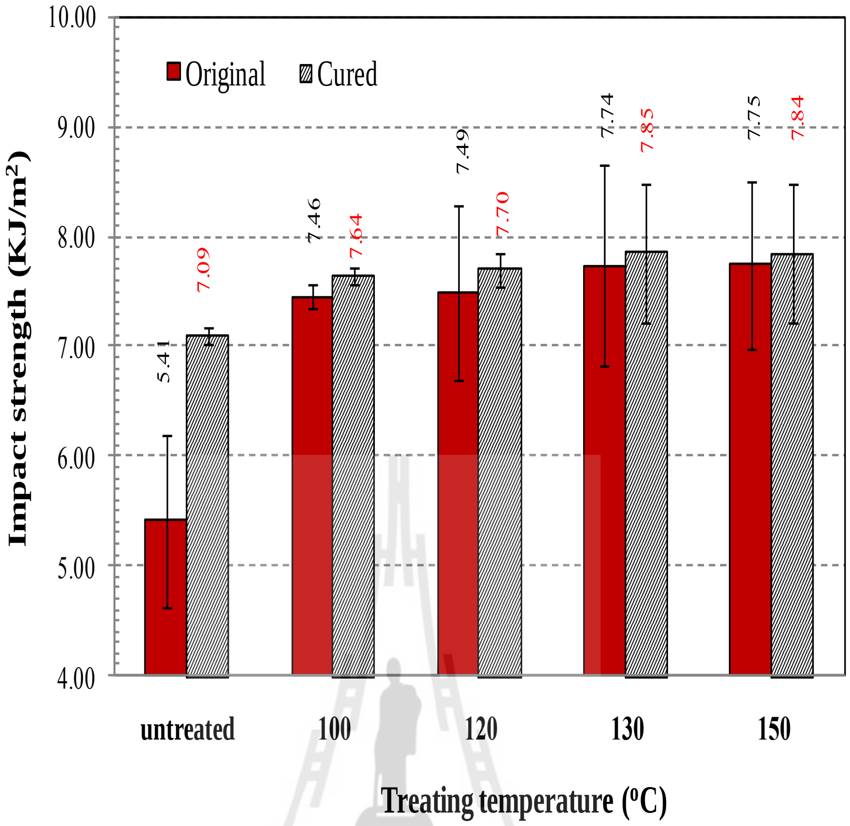


Figure 4.15 Effect of surface treatment temperature on the notched impact strength of HDPE/PTFE blends

4.5.8.6 PTFE treatment temperatures and the surface tension

The relationship of surface tension, by mean of water drop diameter ratio, of HDPE/PTFE blend and conditioning temperature of PTFE using DCP for the original and cured blends are summarized in Table 4.17. Figure 4.16 is the alternate test data presentation using graphical comparison. In according to the test results, both before and after sauna incubation, it is observed that there are ultra marginally changed in the water drop ratios of the blend samples compounded using the surface treated PTFE filler. One quite obvious seen is that the ratio of the blend derived from the PTFE without DCP treatment is higher than the DCP treated ones. Closer analyzing the blends obtained from the DCP treated PTFE filler at the peroxide decomposition temperature from 100, 120, 130 and 150°C, the ratio figures manifest that there is absolutely no effect of the temperature on the surface tension of the blend materials. The ultra tiny deviation of the ratio figure would be due to the systematic error, or standard deviation, of the test measurement. The test result also indicates that the water drop ratios of the blends specimen are lower after undergoing the moisture incubation at 65°C for more than 12 hours.

As state throughout this research study, the water drop diameter ratio smaller than 1.00, it indicates lower surface tension between water and the surface of the polymeric sample than the tension on the Teflon/Fiber Glass sheet. Regarding to the measurement outcome from this study section, the surface tension of the HDPE/PTFE blend having the PTFE content of 20 phr before sauna incubation is higher than the tension of the PTFE sheet. After curing the sample in the sauna oven, the surface tension of the blend sample is lower than the Teflon sheet. There is no significant improvement of the surface tension by increasing the free radical treatment temperature of PTFE particle before blending with HDPE what so ever. Comparing between using PTFE with and without DCP treatment, it seems to be that the surface tension of the treated PTFE/HDPE blend is lower than the sample using PTFE without DCP treatment. The lower in the surface tension by either surface treatment of DCP or sauna incubation of the treated PTFE/HDPE blends would be explained by interfacial enhancement between matrix and the PTFE filler. Normally, better interfacial adhesion between those two phases would create tighter gaps, internal crack, between the phases. As the improvement, lower in the capillary force of the liquid would be experienced. It means that lower in the surface tension of the liquid on the material surface is achieved, liquid can easily roll over. Conditioning the surface of PTFE using free radical decomposed from DCP before blending with HDPE and incubation of the injected blend sample would reduce the internal cracks, better interfacial adhesion, between the HDPE matrix and PTFE filler. Consequently, the lower in the surface tension of the polymeric material is accomplished.

Table4.17 PTFE surface treatment temperatures and the ratio water drop diameter ratio of HDPE/PTFE blends

Treating Temp. (°C)	D_{sample}/D_{PTFE}	
	Original	Cured
untreated	1.06±0.07	1.01±0.04
100	1.04±0.04	0.96±0.07
120	1.06±0.05	0.99±0.04
130	1.06±0.02	0.92±0.05
150	1.09±0.05	0.91±0.09

4.5.8.7 PTFE treatment temperatures and abrasion properties

The wear resistance, by mean of % weight loss, of HDPE/PTFE blends derived from untreated and DCP treated at the given temperatures, both original and cured samples, are summarized in Table 4.17 and the plot of the % weight loss of the blends with temperatures are presented in Figure 4.16. From results obtained, it is seen that the % weight loss is slowly decreased with increasing the decomposition temperatures of DCP. As expected, it is also noticed that the sauna incubation had improved the surface abrasion of the blends. The distinctive abrasive values are found when untreated PTFE was blended with HDPE. The % weight lost of the untreated PTFE/HDPE blend is higher than the blends derived from DCP treated PTFE regardless to the temperatures.

Taken the abrasive testing result found above, it could state that the rising temperature used for free radical surface treatment of PTFE by using DCP has no significant effect to the HDPE/PTFE blends. However, when compare between non treated and treated the surface of PTFE, the study indicates that the % weight lost of the blend using the treated PTFE were much higher than the material without free radical treatment. So, it could suggest that the surface of PTFE was chemically or physically modified by the decomposed free radical. Consequently, the interfacial adhesion between matrix HDPE phases and dispersed PTFE particle is enhanced by surface therapy. Moreover, the superiority in the surface wear properties is achieved by the sauna treatment. Regarding to the temperatures applied for decomposition of DCP, the outcome implies that the temperatures ranging from 100^{o}C to 150^{o}C, as experimented in this study, had no significant effect by mean of the surface improvement of PTFE. Hence, there was no obvious change in the abrasive resistance of the HDPE/PTFE blends obtained.

Table 4.18 Treating condition and abrasive resistances of HDPE/PTFE blends

Treating Temp. (^{o}C)	**Weight loss (%)**	
	Original	Cured
untreated	0.57±0.09	0.50±0.05
100	0.40±0.08	0.22±0.03
120	0.27±0.04	0.21±0.02
130	0.27±0.04	0.21±0.04
150	0.26±0.06	0.22±0.02

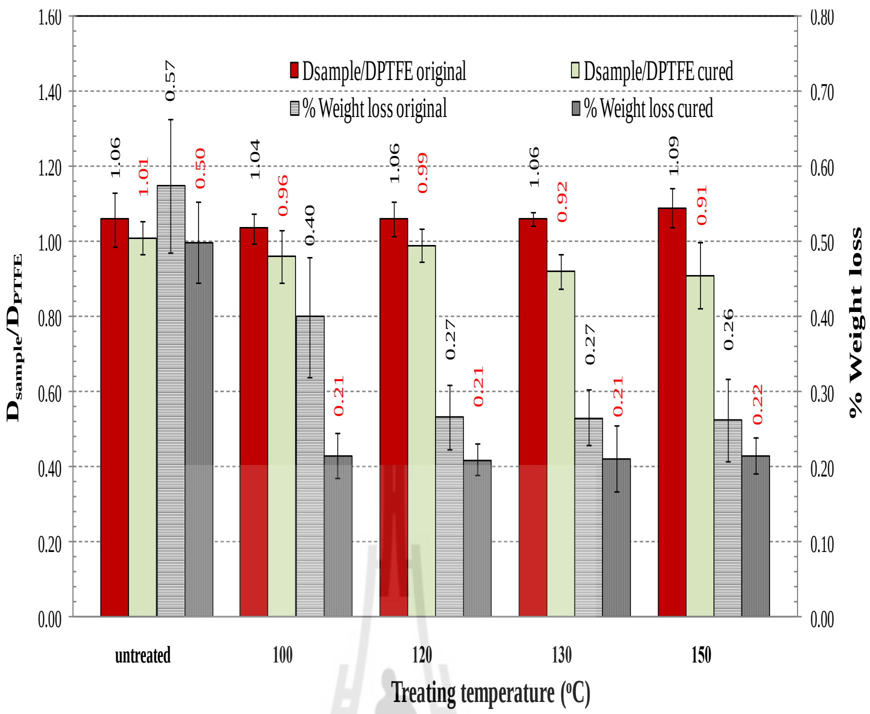


Figure 4.16 Decomposition temperatures of DCP and surface properties of HDPE/PTFE blends

4.5.8.8 Morphological investigation

From the above discussions, there are superior in the properties of surface treated PTFE particle blend with HDPE than the untreated one. The better interfacial bonding between surface treatment of PTFE and HDPE matrix was gathered into explanation. Therefore, the fractured morphology of those blends must be verified. SEM photographs at X1000 of the fractured impact specimens; untreated PTFE and, DCP treated at 100°C and 130°C, are illustrated in Figure 4.17 (***a***) to 4.17 (***f***), respectively. The PTFE particle pullout and phases interfacial adhesion are obviously observed from the SEM photographs for all specimen. Large number of the pullout traces and also bigger gaps between the matrix and dispersed particle means poor interfacial adhesion between HDPE matrix PTFE particles. Lower properties of the blend would be expected.

According to the SEM observation, the obvious instant evidence, without the personal bias, is that there is less pullout traces when the samples undergone sauna treatment, cured sample. It refers that the condensation reaction between silane and moisture molecules, DCP/silane crosslink system added, during the incubation process had somehow introducing the chemical/mechanical interlock between matrix and the filler. Then, the interlock would inhibit the crack propagation. The properties of the blends would be enhanced. Consideration between untreated and DCP treated PTFE, Figure 4.17 (***a***) and (***b***), and Figure 4.17 (***c***) to 4.17 (***f***), it is noticed that the less tendency of the PTFE pullout is evidenced for the DCP treated samples especially when looking on the sample after undergoing the sauna incubation. However, when comparing the samples obtained from DCP treatment at 100^{o}C and 130^{o}C, Figure 4.17 (***c***-***d***) and 4.17 (***e***-***f***), there seem no differ in the pullout phenomenon. From the SEM investigation, it reinforces the statement that surface treatment of PTFE by using free radical decomposed from the DCP shows, one way or another, the advantage in the surface properties PTFE. The treatment introduces the better interfacial property with the HDPE matrix. Consequently, better interfacial bonding and further mechanical properties of the PTFE/HDPE blends is resolved.

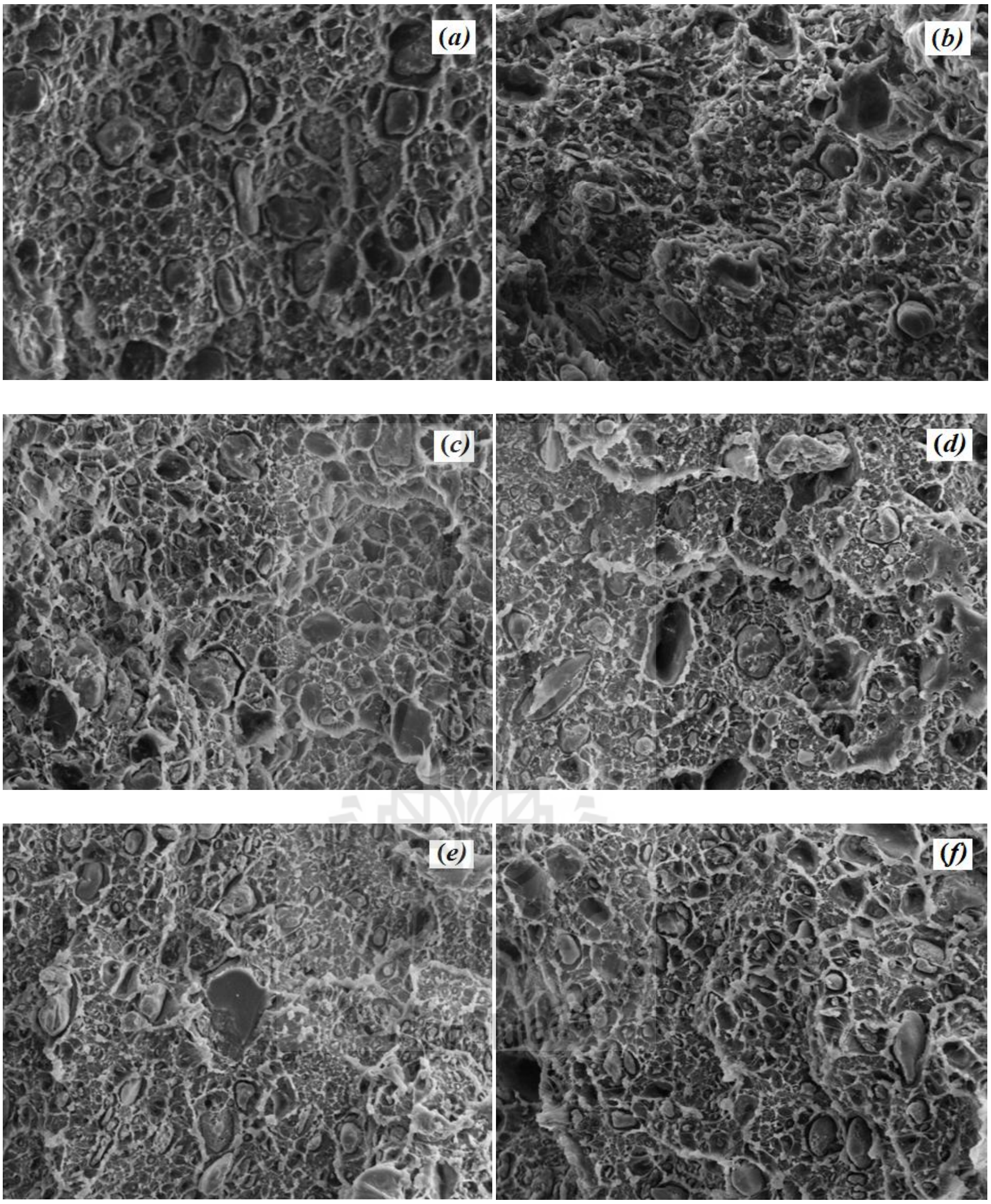


Figure 4.17 SEM micrographs of HDPE/PTFE; (***a***) untreated PTFE (original), (***b***) untreated PTFE (cured) and treated PTFE at (***c***) 100°C (original), (***d***) 100°C (cured) (***e***) 130°C (original) and (***f***) 130°C (cured), respectively.

From the study of the effect of temperature on the free radical surface treatment of PTFE by using DCP before blending with HDPE, the results concluded that the decomposition temperature of DCP during the treatment had no significant effect of the final HDPE/PTFE blend. But, the surface of PTFE was enhanced and then better interfacial adhesion with HDPE matrix than the non treated PTFE was observed.

4.6 Conclusion

Increasing the silane ratio in the silane/DCP crosslink system added into the HDPE/PTFE blends, the test results found that the MFI of the blends did not increase with increasing the silane coupling agent. The HDT of the original samples were also decreased with increasing the silane loading but after undergoing the sauna treatment the HDT was slightly increased with more of silane added. However, at the given amount of silane, the HDT of the cured sample was significantly higher than the original sample. For the mechanical properties of HDPE/PTFE, the results were reviewed that that more flexible material, or softer, were found when increasing in the silane to DCP ratios. The tensile properties were also trend to decrease with increasing the amount of the silane. On the other hand, the impact strength of the blends was higher, softer material, when the silane used was increased. The dilution effects from the liquid silane were taken into the explanation for the mechanical properties dependency of the silane. The surface tensions of the film samples did not depend on the amount of silane added. The surface tension, investigated by the water drop ratio, was almost constant for all samples. The superior in the wear of the samples was found after the sauna treatment at 65^{o}C for more than 12 hours.

For the effect of temperature on the surface treatment of PTFE by free radical decomposed from DCP before blending with HDPE, the results concluded that treatment temperatures of PTFE did not have the significant effect on the mechanical properties what so ever on the HDPE/PTFE blend. However, according to the investigation, the surface of PTFE was noticed to be enhanced when comparing with the surface of PTFE without the treatment. Better in the interfacial adhesion between HDPE matrix and treated PTFE were evidenced.

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CHAPTER V

EFFECT OF UHMWPE TOUGHENER ON THE CROSSLINKED HDPE/PTFE BLEND

5.1 Abstract

The main aim of this study was to improve the toughness HDPE/PTFE blend by incorporating ultra high molecular weight polyethylene (UHMWPE). UHMWPE was added into HDPE/PTFE blends at the content of 5 to 25 phr with corresponded with HDPE. The results showed that at higher UHMWPE content, above 5 phr, the mechanical properties especially flexural and tensile were decreased with increasing the UHMWPE contents. However, the impact strength was increased with increasing the UHMWPE addition. The increasing in the melt viscosity by adding the ultra high polymer and hence retarding the melt mixing for the added ingredient was taken into explanation for the diminishing in the flexural and tensile properties and minor increase in the impact strengths of the HDPE/PTFE/UHMWPE blends. The trade-off between toughness improvements of the HDPE/UHMWPE blend matrix, high melt viscosity of the blend matrix and, consequently, poor dispersion and insufficient adhesion between PTFE and the blend matrix must be taken into consideration for the blending purpose. General speaking, the negative effect derived from adhesion was dominated over the toughness of the blend matrix especially at the high UHMWPE content.

The effect of HDPE/UHMWPE master batching temperatures was experimented and resolved. It was found that better dispersion of UHMWPE in HDPE was obtained by using UHMWPE/HDPE master batch pellet. UHMWPE was partially fused with HDPE matrix phase by direct powder blending with poor dispersion. Consequently, incompetency in the toughness was obtained. There was no significant effect of the UHMWPE/HDPE master batching temperatures, at 200^{o}C, 240^{o}C and 280^{o}C, on the properties of HDPE/UHMWPE/PTFE blends. The fusion and also dispersion of the UHMWPE within the HDPE matrix in the final blends were relatively similar. Consequently, there were no major differences in the properties of the HDPE/UHMWPE blend.

5.2 Introduction

Ultra high molecular weight polyethylene (UHMWPE) has the remarkable properties of excellent abrasion resistance, impact resistance, fatigue resistance, and chemical resistance, and it is commonly defined as one of the engineering polymers. However, the high molecular weight polyethylene (UHMWPE) is normally difficult to melt and provide extremely high melt viscosity, which prevents its flow in conventional techniques of polymer processes. This is because in practice, this material does not flow, thereby limiting its applications. In this context, the mix between the two polymers, HDPE and UHMWPE, is a very interesting alternative since it has the potential to combine the excellent toughness property of UHMWPE and the good process ability of UHMWPE. The basic idea is to add as much UHMWPE to HDPE as possible, taking the advantage of both; the process ability of UHMWPE under conventional techniques and the outstanding wear and mechanical performance of HDPE. These blends have been extensively studied which adds to the knowledge of various aspects of the behavior of UHMWPE under abrasion and wear in various conditions, especially for the application aspects. In this study, the main aim is to improve the toughness HDPE/PTFE blend by blending the matrix with UHMWPE.

5.3 Research methodology

5.3.1 Polymeric materials and chemical ingredients

High density polyethylene (HDPE, EL-Lene H5814J), is general purpose high density polyethylene resin that suitable for injection molding process. It is used as the main polymer matrix. This processing graded HDPE has good flow ability and designed for high productivity with good toughness product. It is kindly supplied from SCG-Chemical Co., Ltd. The typical properties of the HDPE matrix used in this study available from the manufacturer data sheet are summarized in Table 5.1.

Table 5.1 Properties of high density polyethylene (EL-Lene H5814J)

Properties	**Test Method**	**Value, Unit(SI)**
Melting Temperature	ASTM D2117	131°C
Melt Flow Index	ASTM D1238@190/2.16	14 g/10min
Notched Izod Impact	ASTM D256	2 kJ/m^2
Tensile Strength at Yield	ASTM D638@50 mm/min	27.5 MPa
Elongation at Break	ASTM D638@50 mm/min	620%
Flexural Modulus	ASTM D790	1225 MPa
Heat Deflection Temperature	ASTM D648@0.455 MPa	75°C

PTFE, Zonyl® MP 1300 fluoroadditive, is a free flow white powder designed for using as an additive in other materials to impart low surface energy and other fluoro polymer attributions. It is available from DuPont® and it is employed as dispersed phase. According to the manufacturer data sheet provided, the powder has the average particle size of 12 μm. Other properties of the powder are listed in Table 5.2.

Table 5.2 Properties of Poly(tetrafluoroethylene), Zonyl® MP 1300.

Properties	**Test Method**	**Value, Unit**
Melting Temperature	ASTM D4894	325±5°C
Particle Size Distribution	Laser Microtrac	12 μm
Specific Surface Area	Nitrogen Adsorption	1.5-3.0 m^2/g
Average Bulk Density	ASTM D4894	0.425 kg/l

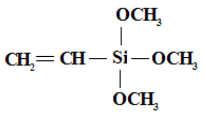
Fine powder of Asahi Kasei Sunfine ultrahigh molecular weight polyethylene (UHMWPE), UH 900, is added into HDPE compound to enhance the toughness and also the surface properties. The properties of the powder that are provided by the supplier and it are presented in Table 5.3.

Table 5.3 Properties of Asahi Kasei Sunfine UHMWPE, UH 900

Properties	**Test Method**	**Value, Unit(SI)**
Melting temperature	DSC method	136°C
Melt density	JIS K 7112	940 kg/m^3
Izod Impact	JIS K 7111	None folding
Tensile Strength at Yield	JIS K 7161	24 MPa
Elongation at Break	JIS K 7161	330%
Flexural Modulus	JIS K 7171	1100 MPa
Heat deflection temperature	JIS K 7191	85°C

Low viscosity and water clear liquid vinyl trimethoxy silane (VTMS), commercialized as Silquest® A 171, is used as crosslink system in conjunction with peroxide through the moisture incubation or sauna treatment. The chemical structure and physical properties of the liquid silane is given in Table 5.4. The chemical is directly used without further dilution and purification.

Table 5.4 Properties of VTMS (Silquest® A171)

Properties	**Value, Unit**
Chemical structure	 $CH_2{=}CH{-}Si(OCH_3)_3$
Boiling point	122°C
Specific gravity, 25°C	0.967 g/ml

Low melting temperature, <50°C, solid dicumyl peroxide (DCP) flake is employed as free radical generator. It is a commercial grad and available throughout the rubber chemicals suppliers. The chemical formula of this peroxide is shown in Figure 5.1. Again, it was used without further purification. It has low melting point, slightly above 50°C. It is normally decomposed and generated quit stable free radical at the temperature above 120°C.

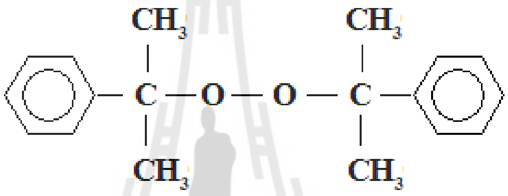


Figure 5.1 Chemical structure of dicumyl peroxide ($C_{18}H_{22}O_2$)

5.3.2 Melt mixing of HDPE /PTFE/UHMWPE blends

The UHMWPE was used in form of master batch with HDPE. It is done in order to; (*i*) ease of solid flow of UHMWPE in the feed hopper and (*ii*) reducing the melt viscosity of the long chain polymer during blending process at low temperature. The master batch melt blending between HDPE and UHMWPE at 60 phr of UHMWPE was prepared by in co-rotating twin screw extruder at 240°C. The master batching was carried out at screw speed of 10 rpm and the barrel temperature of 240°C for all zones. Mixing at temperature below 240°C, the high molecular weight chain was not be completely soften and incorporated with HDPE. Hence, it was behave like disperse polymer particle in the HDPE matrix phase. The well mixing

HDPE/UHMWPE master batch strand was granulated by the pelletizer. It was used as toughener by dilution into the desired concentration.

The PTFE powder was pretreated with silane/DCP as batch wise process in the internal mixer. The calculated amount, with respected to 100 g of PTFE powder, of 0.5 phr of DCP was priory dissolved in 1 phr of silane. The clear solution was promptly added into the PTFE powder in the mixing chamber equipped with the roller rotors. The surface treatment was performed at 100^{o}C and rotors speed of 80 rpm for 5 minutes. The treated powder was emptied and stored in tightly sealed container for at least overnight.

The melt mixing procedures between HDPE, treated PTFE and UHMWPE master batch conducted in this research work is schematically illustrated in Figure 5.2. HDPE was pre dried in the vacuum oven at 80^{o}C for 2 hours. The pre calculated amount of UHMWPE master batch, HDPE, treated PTFE and the rest of the chemical ingredients were brought into the container. The solution of the desired amount of DCP and silane was incorporated into the solid ingredients and vigorously stirred. The typical UHMWPE concentration in the HDPE/PTFE blends was 5, 10, 15, 20 and 25 phr. The well mixed constituent was fed into the twin screw barrel via the single screw type feeder. The melt blending was performed at 190^{o}C for all barrel zones and the output rate was controlled by the screw rotation at 10 rpm. The polymer blend strand was allowed to cool down in the atmospheric and crushed into the pellet form by using the machine crusher.

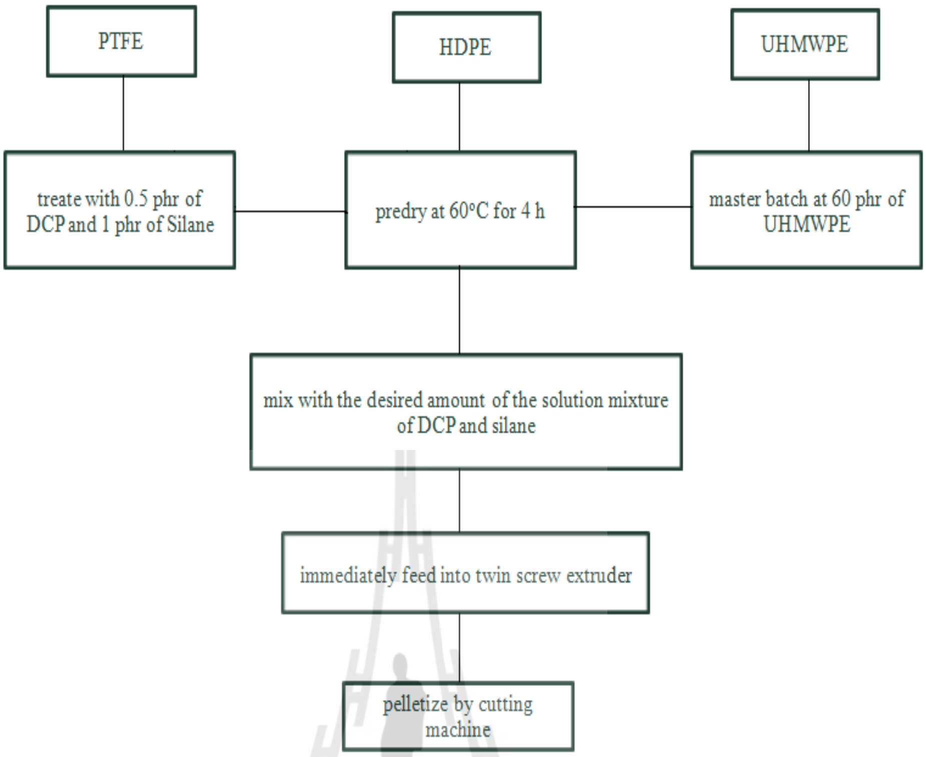


Figure 5.2 Schematic diagram of HDPE/PTFE/UHMWPE blending procedure

5.3.3 Test Specimen Preparation

5.3.3.1 Sample injection molding

The tensile, flexural and impact testing samples were prepared by injection molding using a reciprocating screw injection molding machine, CHUAN LIH FA T80. The temperatures profile for molding was 190, 200, 210 and 220^{o}C from feed to nozzle, respectively. The family and artificially balanced two plate mold consisted of two dumb bells, type I and type IV, one rectangular bars for flexural and HDT testing and one short rectangular bar for impact testing, was employed. The size and shape of the injected specimens were in accordance with ASTM regulations. The temperature of water mold coolant was carefully controlled at 30^{o}C. The injection pressure was electronically controlled at 80% of the maximum machine capacity. The injected samples were divided into 2 sets. The first one was allowed to anneal at room temperature overnight and they was categorized as “**original**” sample by definition in this research work. The later was undergone post curing in the moisture saturated oven at 65^{o}C for more than 12 hours. The incubation temperature was close to the T_g of HDPE used, therefore allowing the moisture molecule to easily penetrate into the free space of the chain. Hence, the completion of the siloxane/moisture condensation could be accelerated and succeed. These treated specimens were classified as sauna cured or shortly as “**cured**” sample.

5.3.3.2 Thick film preparation

Thick film samples for the abrasion testing were obtained by hot compression process. A few grams of the compound pellet were placed in between two PTFE/Glass woven sheets. The set up was transferred into the plat molds. The polymer was preheated at 200^{o}C for 10 min then slowly pressed at 110 MPa for 6 min. The pressed film was immediately removed and allowed to cool down at room temperature. The smooth film with the approximate thickness of 0.4 mm was obtained. The abrasion test specimen was scissor cut into the disk shaped with the diameter of 4.5 cm. The centered hole was punched. Similarly, the sheet films were also divided into 2 set of samples; original and sauna cured, respectively.

5.4 Properties measurement and analysis

5.4.1 Melt flow index

The rheological property by mean of melt flow index (MFI) was conducted. The MFI of the HDPE/PTFE pellet was tested in accordance with ASTM D 1238 using the Kayeness melt flow indexer model 4004 at standard test condition of 230/5.0. The obtained pellet samples was vacuum dried in the oven at 80°C for at least 2 hours to eliminate the possible moisture residual. The polymer pellet was allowed to completely molten at 230°C for 240 seconds and it was driven through the capillary die (Ø 1 mm.) using piston load of 5.0 kg. Three cuts were performed at the precise cut times of 30 seconds. The extrudate was weighed and computed into the melt flow index in the standard unit of g/10min.

5.4.2 Physical properties testing

5.4.2.1 Impact strengths

Impact strengths of the HDPE/PTFE/UHMWPE blends were tested in according with ASTM D 256 in the Izod mode. The injection molded specimen obtained with the dimension of 12x50x3 mm. was notched using the notching machine. The identical injected samples were tested without notching. Notched and unnotched impact strengths were conducted at room temperature using the impact pendulum with impact energy of 2.7 Joule for the notched and 5.4 Joule for the unnotched samples, respectively. The impact values were reported as impact strength, kJ/m^2, that were calculated from impact energy required for completely breaking the sample over the cross section area at fractured area. At least five samples were tested for each polymer sample and the average value were obtained and reported in this experimental study.

5.4.2.2 Flexural properties

Flexural properties by mean of the strength and modulus of the HDPE/PTFE/UHMWPE sample were examined in accordance with ASTM D790. The obtained injection molded sample with the dimension of 12x120x3.5 was performed. Instron universal testing machine, model 5565, with the load cell of 5 KN and three point bending test fixture with span length of 56 mm, approx. 16 times of the thickness, was employed. The crosshead speed of 50 mm/min was constantly controlled during the bending load. The test specimen was placed plat wise to the bending load. The test was conducted at room temperature in normal atmospheric condition. The flexural strength and modulus were computerized using the following equation (5.1) and (5.2), respectively. At least five samples were conducted for each polymer sample and the average value were obtained and reported in this study.

$$\textbf{Flexural Strength} = \frac{3PL}{2[bd]^2} \tag{5.1}$$

Where: P = load at a given point on the load-deflection curve (N)

L = support span (mm)

b = width of beam tested (mm)

d = depth of beam tested (mm)

and

$$\textbf{Flexural Modulus} = \frac{L^3 m}{4(bd)^3} \tag{5.2}$$

Where: L = support span (mm)

b = width of beam tested (mm)

d = depth of beam tested (mm)

m = slope of the tangent to the initial straight line portion of the load-deflection curve (N/mm) of deflection.

5.4.2.3 Heat deflection temperature

Heat deflection temperature (HDT) of the HDPE/PTFE/UHMWPE blend was conducted with the ASTM D 648. The sample was tested in the edgewise position, with the support span length of 100 mm. The simple beam with the standard load applied at its center to give maximum stress of 0.455 MPa or 66 psi was followed. The testing machine from Atlas, model HDV 1, was employed. The raising temperature at a uniform rate of 2±0.2^{o}C/min was assigned. Liquid silicone oil was used as heating transfer media. The HDT value was reported in degree Celsius (^{o}C) as soon as the specimen had been deflected to 0.25 mm or 0.01 inch that monitored by the dial gauge. This temperature was recorded as the deflection temperature under the assigned standard flexural load of the test specimen. Three samples were examined and the average value was reported.

5.4.2.4 Tensile properties

Tensile properties of HDPE/PTFE/UHMWPE blends were examined using an Instron universal testing machine, model 5565, with a load cell of 5 kN, crosshead speed of 50 mm/min and a gauge length of 80 mm. Tensile tests were performed according to ASTM D638. The dimension of the molded dumbbell shaped specimens, type I, with 12.7 mm in width at narrow section, 20 mm in overall width, 80 mm in gauge length, 165 mm in overall length and approx. 3.5 mm in thickness was used for performing the test. Five samples were tested in each blend sample. The calculated tensile strength (N/m^2 or Pa) was given by dividing the maximum load, in Newton force (N), by the average original cross sectional area in the gage length segment of the specimen in square meters (m^2). The modulus of elasticity value was performed by extending the initial linear portion of the load extension curve and dividing the difference in stress corresponding to any segment of section on this straight line by the corresponding difference in strain. Percentage elongation at break was computed by reading the extension at the yield point and then dividing that extension by the original gage length and multiplies by 100.

5.4.3 Surface properties observation

5.4.3.1 Wear testing

Wear ability of the HDPE/PTFE/UHMWPE blend by mean of abrasion testing was investigated. The standard method namely ASTM D 4060 Abrasive Wear Testing, was followed. It is the measurement of the weight loss under the specified test conditions. In this study, specimens were abraded at 500 rounds of rotation under the constant load at 0.25 kg and H-18 abrader type. The weight loss of the sample was recorded as the below calculation. Three circular HDPE/PTFE/UHMWPE blend films prepared by the procedure describe in section 5.3.3.2 was employed. Each of specimens was individual tested. The averaged the weight loss was gathered and presented.

$$\textbf{\%Weight loss} = \left[\frac{\text{Weight before test} - \text{Weight after test}}{\text{Weight Before test}}\right] \text{x } 100 \qquad (5.3)$$

5.4.3.2 Surface tension observation

The surface tension of the polymer film to the liquid is normally tested by surface angle measurement using the appropriate test liquid and laser precision measurement. At the presence time, such expensive equipment is not available in our research laboratory. Attempting to investigate the surface tension of HDPE/PTFE/UHMWPE film was conducted by using the adaptive, or comparative, test method. The deionized water was used as the test liquid. The adopted method to evaluate the surface tension between the test liquid and the surface of the injected blends specimen or film were constructed. The micro pipette with the minimal volume capacity of 20 μl equipped with the micro tip adapter was used for applying the water drop on the film surface. Drops of 1.0 μl of the deionized water through the micropipette were carefully placed onto the cloth dried surface of the blend sample. The diameter of the water drop (D_{sample}) was measured through the optical micro scope and analyzed digitally. The diameter of the water drop on the commercial PTFE/Glass woven sheet (D_{PTFE}) was obtained and used as the referee values. It was assumed that it was measured on the pure surface of PTFE film. Then, the ratio between the diameters of the water drop on the sample divided by the diameter of the drop on the referee PTFE sheet (D_{sample}/D_{PTFE}) was computed according to the equation 4.4. If the computed ratio is higher than 1.0, it means that the diameter of demonized water on the blend sample is larger than on the PTFE sheet. It indicates that the surface tension of the blend sample is higher than the surface tension on the PTFE. Vice versa, if the ratio less than 1.0 is obtained, it reviews that the surface tension of the blend would be lower than the referee PTFE sheet.

$$D_{Sample}/D_{PTFE} = \frac{\text{Diameter of drop on sample}}{\text{Diameter of drop on the standard PTFE sheet}} \qquad (5.4)$$

5.4.4 Scanning Electron Micrograph(SEM)

Morphology of the fractured surface of HDPE/PTFE/UHMWPE obtained from the notched impact testing was pictured using scanning electron microscope (SEM). The broken piece specimen was cut in to small piece to fit the SEM sample holder. It was securely attached onto the sample holder. The samples were coated with layers of gold for 8 minutes by ionization process before analysis. SEM photograph was taken using JOEL machine model JSM6400 at the typical accelerating voltage of 10 keV.

5.5 Results and Discussion

The compound formula for HDPE/PTFE/UHMWPE blends summarized in Table 5.5, it is seen that the UHMWPE content was varied from 5 to 25 phr. Mean while, the DCP, silane and PTFE contents were kept constant at 1.0, 4.0 phr and 20 phr, respectively. The HDPE/PTFE blend without UHMWPE was used for sake of reference material. The standard test results of the blends in corresponding with the UHMWPE addition are being discussed.

Table 5.5 The blend formulation of HDPE/PTFE/UHMWPE blends

Sample	HDPE(g)	PTFE	DCP	Silane	UHMWPE
		(g) (phr)	(g) (phr)	(g) (phr)	(g) (phr)
Blend(UH0.0)	400	80(20)	4(1)	16(4)	-
Blend(UH 5.0)	400	80(20)	4(1)	16(4)	20(5)
Blend(UH 10.0)	400	80(20)	4(1)	16(4)	40(10)
Blend(UH 15.0)	400	80(20)	4(1)	16(4)	60(15)
Blend(UH 20.0)	400	80(20)	4(1)	16(4)	80(20)
Blend(UH 25.0)	400	80(20)	4(1)	16(4)	100(25)

5.5.1 Flow ability and UHMWPE addition

Rheological property by mean of melt flow index (MFI) at 200/5.0 of the UHMWPE toughened HDPE/PTFE blends is summarized in Table 5.6 and also plotted in Figure 5.3. It is seen that the melt flow index of the blend is linearly decreased with increasing amount of UHMWPE. As expected, the flow resistance is increased, lower MFI, when the amount of high molecular weight chain blended is increased. This indicates that UHMWPE is somehow fused with the HDPE. Therefore, the viscosity of the matrix, consequently to blend, would be increased. Higher in viscosity of the blend has two folds effect; pro and con. The melt strength of the polymer will be enhanced and it will be suit for the extrusion based process. Vice versa, the flow resistance is the drawback properties for the injection based fabricators. High injection pressure would be required. Also, the short shot defect would be experienced.

Table 5.6 MFI of HDPE/PTFE/UHMWPE blends

Sample	**MFI@200/5.00**
	(g/10min)
Blend(UH0.0)	0.421±0.032
Blend(UH 5.0)	0.031±0.030
Blend(UH 10.0)	0.031±0.021
Blend(UH 15.0)	0.022±0.006
Blend(UH 20.0)	0.021±0.012
Blend(UH 25.0)	0.019±0.012

5.5.2 HDT and UHMWPE addition

The thermal property of HDPE/PTFE/UHMWPE tertiary blends by mean of heat distortion temperature tested at 455kPa is illustrated in Table 5.7. In comparison between the original and sauna cured blend, it is noticed that the obvious increasing in the HDT after the treatment is evidenced. Consideration the effect of UHMWPE on the HDT of the HDPE/PTFE blends before and after sauna treatment, the results are also graphically shown in Figure 5.3. Within the standard deviation error, it is seen that the HDT of both original and cured samples are marginally decreased with increasing the UHMWPE addition. It could be because of the fact that the HDT of UHMWPE, according to the data sheet is approx. 85^{o}C, more or less in the range of the HDT of HDPE at 75^{o}C. Therefore, adding UHMWPE into the HDPE matrix would not significantly higher the HDT of the blends. However, in the HDPE/PTFE/UHMWPE blend system, if the adhesion between the constituents is not achieved, the incompetency of the service temperature would be resulted. With the assisting of the crystallinity improvement by annealing process at the high temperature and together with the crosslinking of the polymers chain, it would increase in the HDT of the blends as reviewed by the cured samples.

Table 5.7 HDT of HDPE/PTFE HDPE/PTFE/UHMWPE blends

Sample	HDT (°C)	
	Original	Cured
Blend(UH0.0)	64.1±0.4	79.3±0.1
Blend(UH 5.0)	62.8±2.6	77.9±1.8
Blend(UH 10.0)	58.9±0.6	76.9±0.1
Blend(UH 15.0)	58.1±0.6	75.3±1.9
Blend(UH 20.0)	57.3±0.3	75.3±0.9
Blend(UH 25.0)	57.2±0.4	75.2±1.8

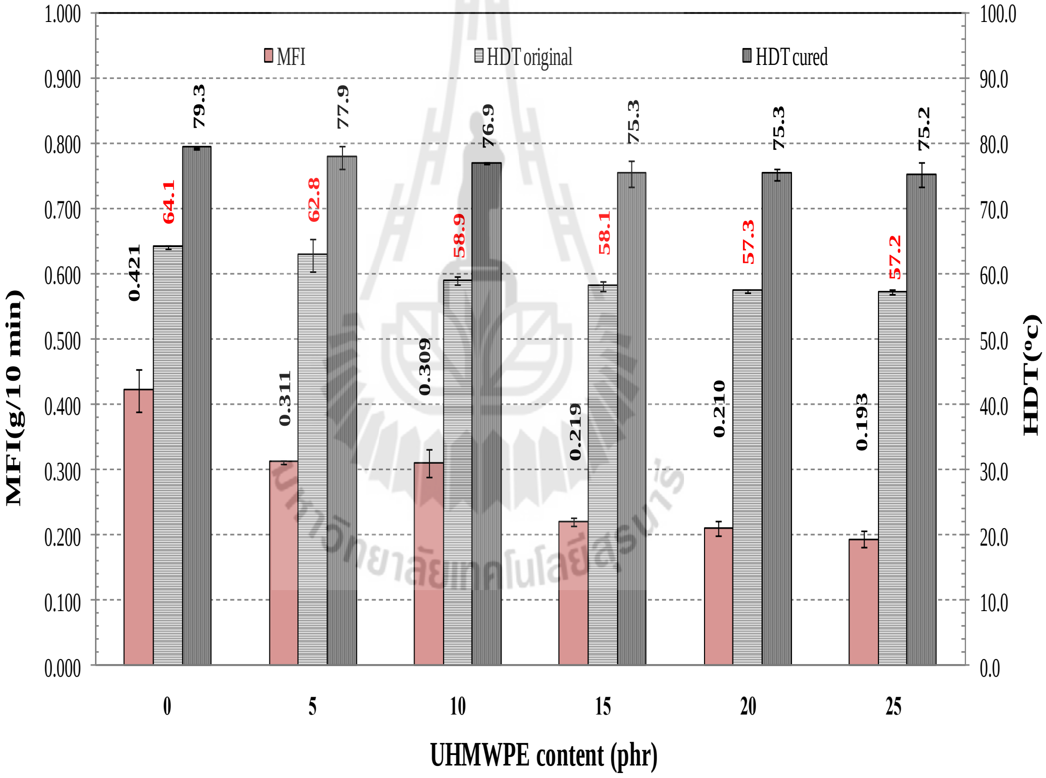


Figure 5.3 MFI and HDT plot of the HDPE/PTFE/UHMWPE blends

5.5.3 Flexural properties and UHMWPE contents

The test values of the flexural strength and modulus of HDPE/PTFE/UHMWPE blends are summarized in Table 5.8 and they are plotted with respect to the UHMWPE concentration given in Figure 5.4 for the original and sauna cured samples, respectively. It is indicated that flexural strength is almost independence with the amount of ultra high polymer addition. The maximum flexural strength of the blends is found in the sample without UHMWPE addition for both original and incubated blends. It was expected that, with good blending between HDPE and UHMWPE, the fracture toughness of the blend would be enhanced by the UHMWPE toughener. But, the constant in the flexural strength obtained with addition of UHMWPE is might be two folds explanation; the adding the portion of high chain length of UHMWPE into the blends would inhibit good dispersion of the blending ingredient, consequently, there is no fusion of the high molecular weight polymer during melt mixing. Recalling from the experimental section, the melt blending temperature was controlled at 190^{o}C. While, the processing temperature of UHMWPE normally above 300^{o}C, the polymer fusion of this polymer cannot be achieved at the given mixing temperature. As the result, the high molecular weight polymer would only act as the foreign particle in the blend matrix, not the matrix toughener. Accordingly, the bending toughness would be not being improved as increasing the UHMWPE loading. When comparison between original and cured sample at the given UHMWPE dose, it is seen that the strength of cured is higher than the original one. The assisting of prolong annealing condition at the high temperature of the blends would introduce the chain crystallinity into the material. Hence, the strength of the blends would be increased.

For the flexural modulus values, the similar trend as seen in the strength is noticed. It is seen that the modulus of the HDPE/PTFE blend with different concentration of UHMWPE shows no clear relationship with the amount of UHMWPE used for both type of samples. The same hypothesis; the phase separation between UHMWPE particle and the matrix due to the increasing in the molar mass portion and/or chain entanglement by adding UHMWPE could be engaged into the explanation. This piece of statement will be clarified by the SEM investigation.

According to the flexural properties obtained in this section, the early conclusion in the term of the toughening effectiveness of the UHMWPE added into the HDPE/PTFE blends could be written. The bending strength of the blends was not enhanced by adding the long chain polymer. High processing of UHMWPE and hence lack of the good blending between HDPE matrix and the added toughener would be responsible for the failure.

Table 5.8 Flexural properties of HDPE/PTFE/UHMWPE blends

Sample	**Flexural strength (MPa)**		**Fluxural modulus (GPa)**	
	Original	Cured	Original	Cured
Blend(UH0.0)	36.68±0.99	38.16±1.30	1.906±0.104	2.034±0.0974
Blend(UH 5.0)	25.59±1.27	29.98±1.17	1.252±0.084	1.470±0.086
Blend(UH 10.0)	25.02±1.03	29.54±0.67	1.230±0.075	1.474±0.047
Blend(UH 15.0)	24.62±0.42	29.49±0.60	1.198±0.034	1.472±0.052
Blend(UH 20.0)	25.96±0.79	29.31±0.17	1.244±0.040	1.456±0.009
Blend(UH 25.0)	25.52±0.32	28.93±0.75	1.214±0.024	1.456±0.043

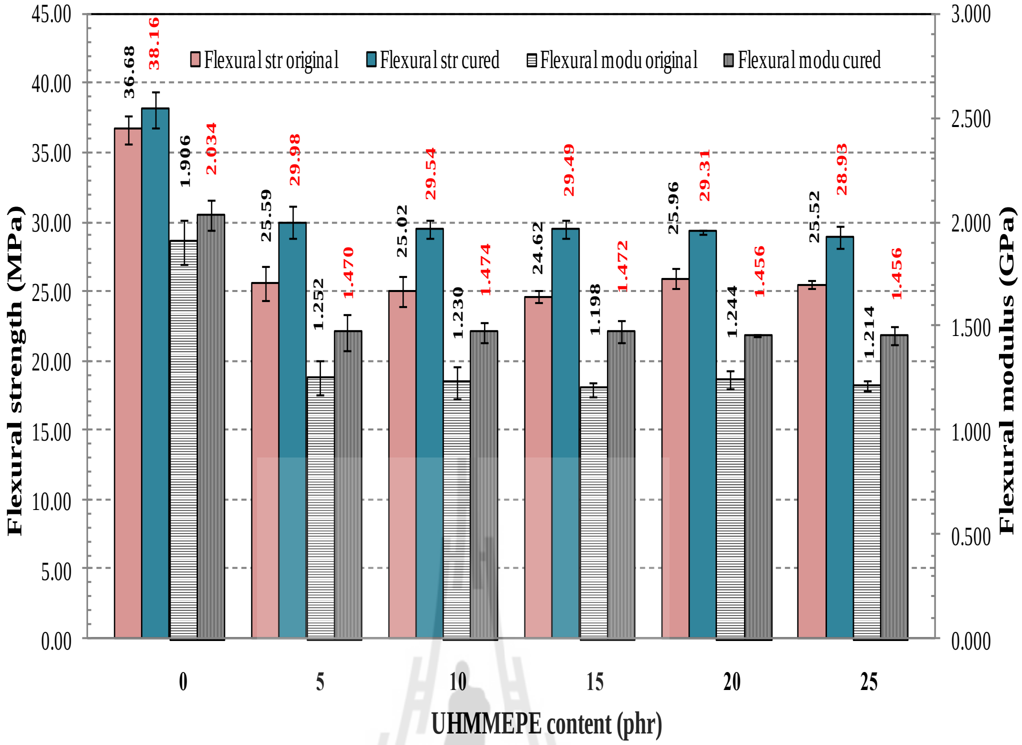


Figure 5.4 Flexural properties HDPE/PTFE/UHMWPE blends

5.5.4 Tensile properties HDPE/PTFE/UHMWPE blends

Tensile properties by mean of strength, modulus and its % elongation at break of HDPE/PTFE/UHMWPE blends at strain rate of 50 mm/min are shown in Table 5.9. Mean while, Figure 5.5 is the plot between the strength and modulus and the UHMWPE contents. From the test values obtained, it is seen that strength and modulus are marginally decreased with increasing the UHMWPE addition but the lower in the values are quite obvious especially at the high UHMWPE contents. Comparing with the system without UHMWPE addition, the strength is much lower but the modulus is much higher by adding the ultra high molecular weight polymer. Apparently at the given UHMWPE concentration, it is also observed that the strength is increased but the modulus is decreased when the sample was treated in the sauna oven.

In Figure 5.6 shows the relationship between % elongations at break and UHMWPE contained in HDPE/PTFE blends for both original and cured samples. The exact trend with the strength and modulus is observed. % elongation of the tertiary blends is almost constant at lower UHMWPE dosage but it is slowly decreased at the content beyond 15 phr. This result indicates that the flexibility of the blend become weaker at high UHMWPE loading. If the compatibility or with good mixing between HDPE and UHMWPE were obtained, the elongation toughness of the material would be better or at least unchanged when compare with the HDPE matrix. From the incompetency of the elongation at break of the blend, especially at high UHMWPE loading, would be caused from the inferior in the adhesion between the HDPE/UHMWPE matrix and the PTFE particle. Increasing in the UHMWPE ratio will increase the viscosity of the blend matrix. Consequently, the adhesion between the PTFE particle and the continuous phase would perhaps become poorer. From the result, it can also be observed that the elongation at break of the blends is not significantly changed via the sauna incubation. Normally, the % break would be vastly decreased with increasing the polymer crystallinity. However from the test figures obtained at the given amount of UHMWPE, there is no obvious trend between the original and sauna cured samples.

General speaking, it can say that the tensile properties of the HDPE/PTFE/UHMWPE blends were inferior with increasing the loading of UHMWPE in the HDPE matrix. The main effects would be the phase separation between HDPE/UHMWPE blend matrix and PTFE particle. Adding more of the high molecular mass polymer into HDPE chain will increase the melt viscosity of the blend. Hence, the dispersion and also the compatibility of the ingredient during the melt mixing would become depleted. Then, the agglomeration of the added particle would be the negative phenomena of the blend and poor adhesion would be resulted.

Table 5.9 Tensile properties of HDPE/PTFE HDPE/PTFE/UHMWPE blends

Sample	Tensile strength(MPa)		Tensile modulus (GPa)		Elongation at break (%)	
	Original	Cured	Original	Cured	Original	Cured
Blend(UH0.0)	22.66±0.26	21.60±0.42	0.762±0.073	0.672±0.051	54.37±3.89	55.77±4.80
Blend(UH 5.0)	19.44±0.91	20.12±0.16	1.326±0.106	0.708±0.025	56.16±2.98	56.01±3.87
Blend(UH 10.0)	18.88±0.46	19.90±0.48	1.270±0.024	0.710±0.026	53.87±1.88	55.99±3.57
Blend(UH 15.0)	18.71±0.57	19.49±0.23	0.976±0.384	0.680±0.029	53.61±1.78	53.56±8.46
Blend(UH 20.0)	18.71±0.27	19.39±0.52	0.662±0.051	0.680±0.028	50.97±0.87	53.89±5.30
Blend(UH 25.0)	18.66±0.46	19.34±0.33	0.632±0.019	0.678±0.044	50.18±3.35	48.12±2.57

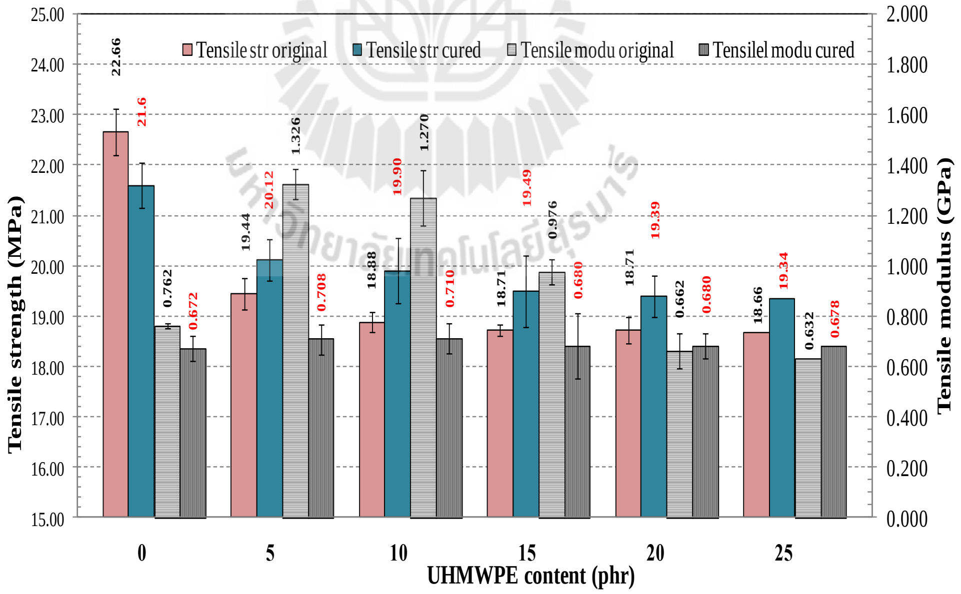


Figure 5.5 Tensile properties of HDPE/PTFE /UHMWPE blends

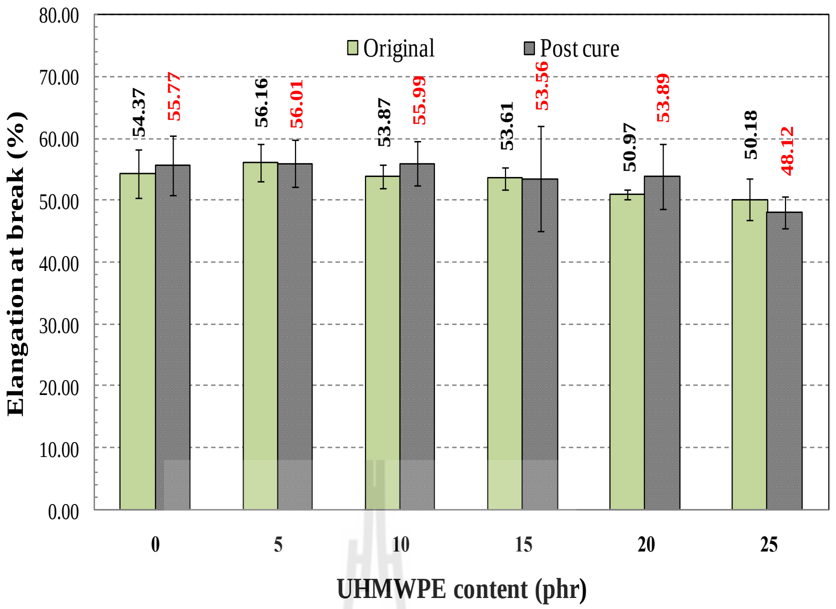


Figure 5.6 % Elongation at break of HDPE/PTFE /UHMWPE blends

5.5.5 Impact strengths and UHMWPE contents

The increasing in the fracture toughness of HDPE/PTFE blend with UHMWPE loading was expected. From the results obtained in Table 5.10 and in Figure 5.7 reveal that the test specimens are not broken at the given pendulum energy of 5.4 J for the unnotched mode of test. Therefore, the comparative between the unnotched impact strength of the blend with increasing UHMWPE loading cannot be discussed. There is no higher energy impactor available in our laboratory.

For notched impact strength testing, as expected, it can be observed that the notched impact strength is increased with increasing the amount of UHMWPE blending for both original and cured samples. According to this study, the maximum strength is found at the UHMWPE content above 20 phr. It indicates that UHMWPE particles are acted as the crake inhibitor. It would absorb energy during the crack propagation. Then, the crake growth would be retarded. If good mixing of the blend is obtained, the superior in the impact strength would be phenomenon. From the result found, the degree of enhancement in the fracture toughness of the blend is quit minimal. It would be traded off by the bad adhesion between the HDPE/UHMWPE blend matrix and PTFE particle. The indicator for this statement will be shown the SEM photograph later on.

Table 5.10 Impact strengths of HDPE/PTFE/UHMWPE blends

Sample	Notched (KJ/m^2)		Notched (KJ/m^2)	
	Original	Cured	Original	Cured
Blend(UH0.0)	4.46±0.11	5.04±0.07	NB	NB
Blend(UH 5.0)	6.02±0.23	6.60±0.23	NB	NB
Blend(UH 10.0)	6.41±0.11	6.80±0.15	NB	NB
Blend(UH 15.0)	6.89±0.30	7.24±0.23	NB	NB
Blend(UH 20.0)	7.22±0.04	7.64±0.22	NB	NB
Blend(UH 25.0)	7.49±0.08	7.52±0.18	NB	NB

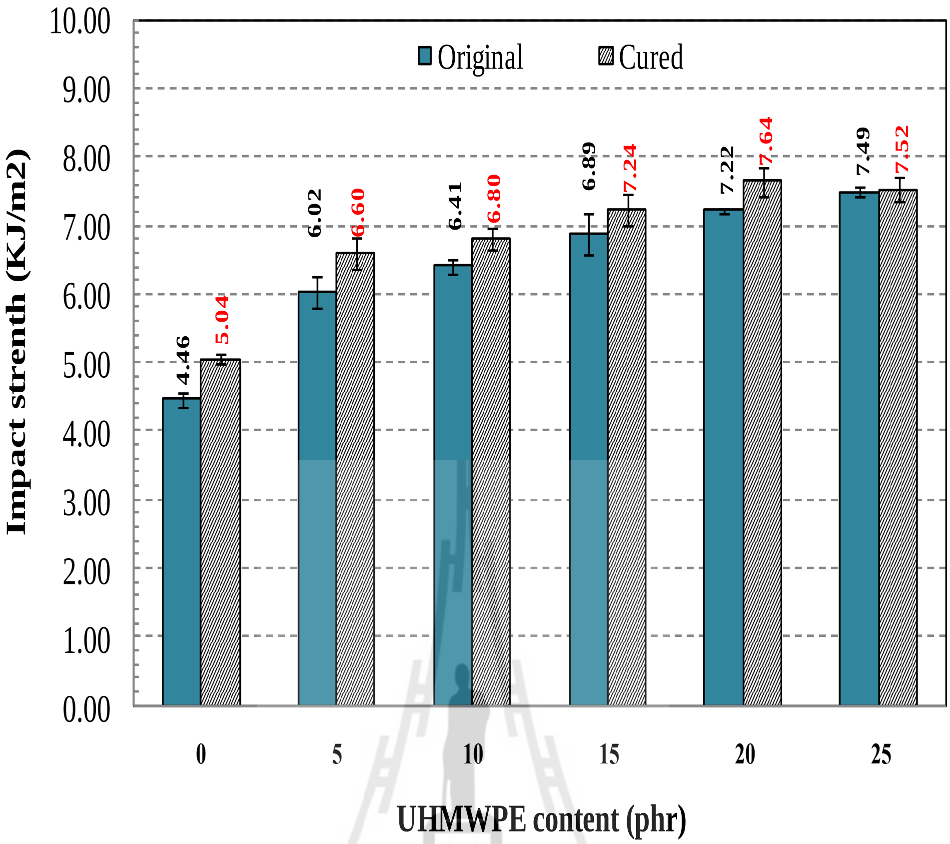


Figure 5.7 Notched impact strength of HDPE/PTFE/UHMWPE blends

5.5.6 Surface properties and UHMWPE contents

One of the main objectives in this research study is manufacturing lower the surface tension of the HDPE/PTFE blend without scarifying the mechanical properties. Good fracture toughness of the material was expected by adding UHMWPE in to the HDPE/PTFE blend. Table 5.11 and Figure 5.8 show the surface properties of the HDPE/PTFE/UHMWPE blends by mean of water drop diameter ratio for the original and cured samples, respectively. It is seen that there are very little changed in the ratio value for both type of samples. For the original sample, it is also seen that the value is above 1.0. The values less than unity are observed in the sauna cured blends at low UHMWPE contents. As mentioned earlier that low surface tension of the blend would be indicated by the ratio less than 1.0. Generally, adding UHMWPE into the HDPE/PTFE blend gives rise to the better tension, especially at high contents, between water and the polymer blends. The capillary effect derived from the spaces, terrible surface adhesion, between HDPE/UHMWPE blend matrix and PTFE particle. The water molecule would be sucked into the gaps and adhere with the surface of the material. The worst adhesion between the blend and PTFE particles the bigger gaps and better surface tension would be become. Curing the sample by the sauna incubation would enhance the PTFE and matrix adhesion. Hence, the number of gaps would be minimal and then less capillary effect is observed.

Table 5.11 Water drop diameter of HDPE/PTFE/UHMWPE blends

Sample	**D_{sample}/D_{PTFE}**	
	Original	Cured
Blend(UH0.0)	1.03±0.42	0.96±0.07
Blend(UH 5.0)	1.03±0.07	0.90±0.01
Blend(UH 10.0)	1.03±0.06	0.90±0.05
Blend(UH 15.0)	1.03±0.05	0.99±0.11
Blend(UH 20.0)	1.05±0.09	1.04±0.04
Blend(UH 25.0)	1.05±0.02	1.04±0.06

5.5.7 Wear resistance and UHMWPE contents

The surface wear resistance of HDPE/PTFE/UHMWPE blends conducted by % weight loss determination for both original and cured samples is presented in Table 5.12 and Figure 5.8, respectively. According to the % weight loss obtained, the dependency of the surface wear properties with the amount of UHMWPE addition is hardly observed. Within the acceptable standard deviation, almost unchanged in the % loss with the UHMWPE loading is indicated. However without the ambiguous judgment, it could say that the surface wear resistance marginally superior at higher UHMWPE loading. Also at the certain amount of high molecular chain incorporation, the superiority in the surface wear properties is achieved by the sauna treatment. In fact from the later SEM evidence, the added UHMWPE can be fused with the HDPE matrix to form the HDPE/UHMWPE blend. UHMWPE itself has the reputation of the one of the polymers with the better surface wear resistance. Accordingly, good blending the long length polymer chain into the HDPE would enhance the wear property. Again, the degree of improving in the properties would be traded off by the inferiority of the adhesion between high viscosity of the blend matrix and the PTFE particle. In the cast of this research study, the surface adhesion enhancement by the sauna treatment would narrow the mentioned negative effect. Therefore, the % weight loss of the HDPE/PTFE/UHMWPE was decreased, better wear resistance, after undergoing sauna incubation.

Table 5.12 Abrasive resistances of HDPE/PTFE/UHMWPE blends

Sample	**Weight loss (%)**	
	Original	Cured
Blend(UH0.0)	0.49±0.07	0.40±0.03
Blend(UH 5.0)	0.49±0.17	0.39±0.16
Blend(UH 10.0)	0.49±0.16	0.38±0.17
Blend(UH 15.0)	0.49±0.21	0.38±0.14
Blend(UH 20.0)	0.49±0.03	0.37±0.24
Blend(UH 25.0)	0.44±0.04	0.35±0.21

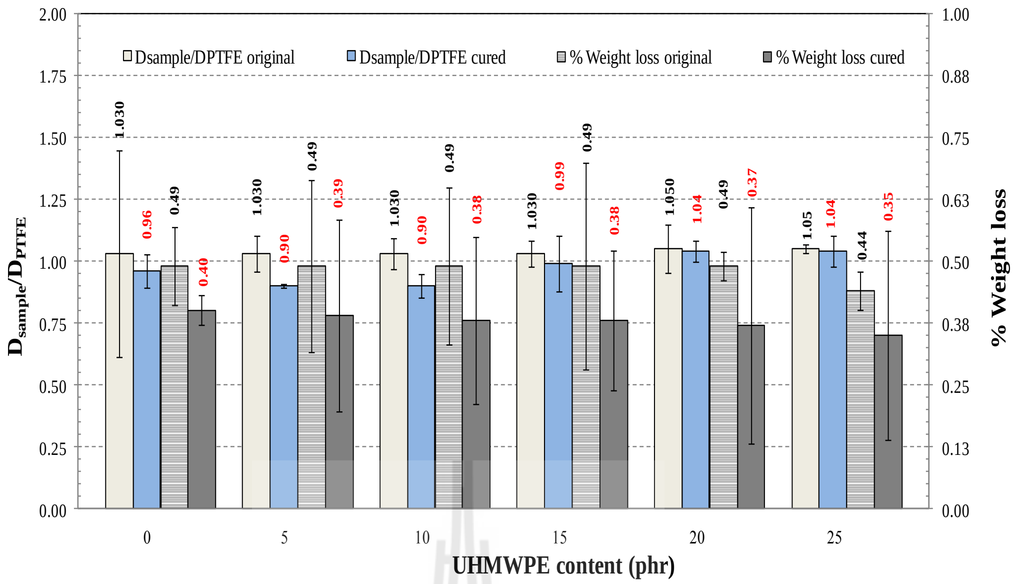
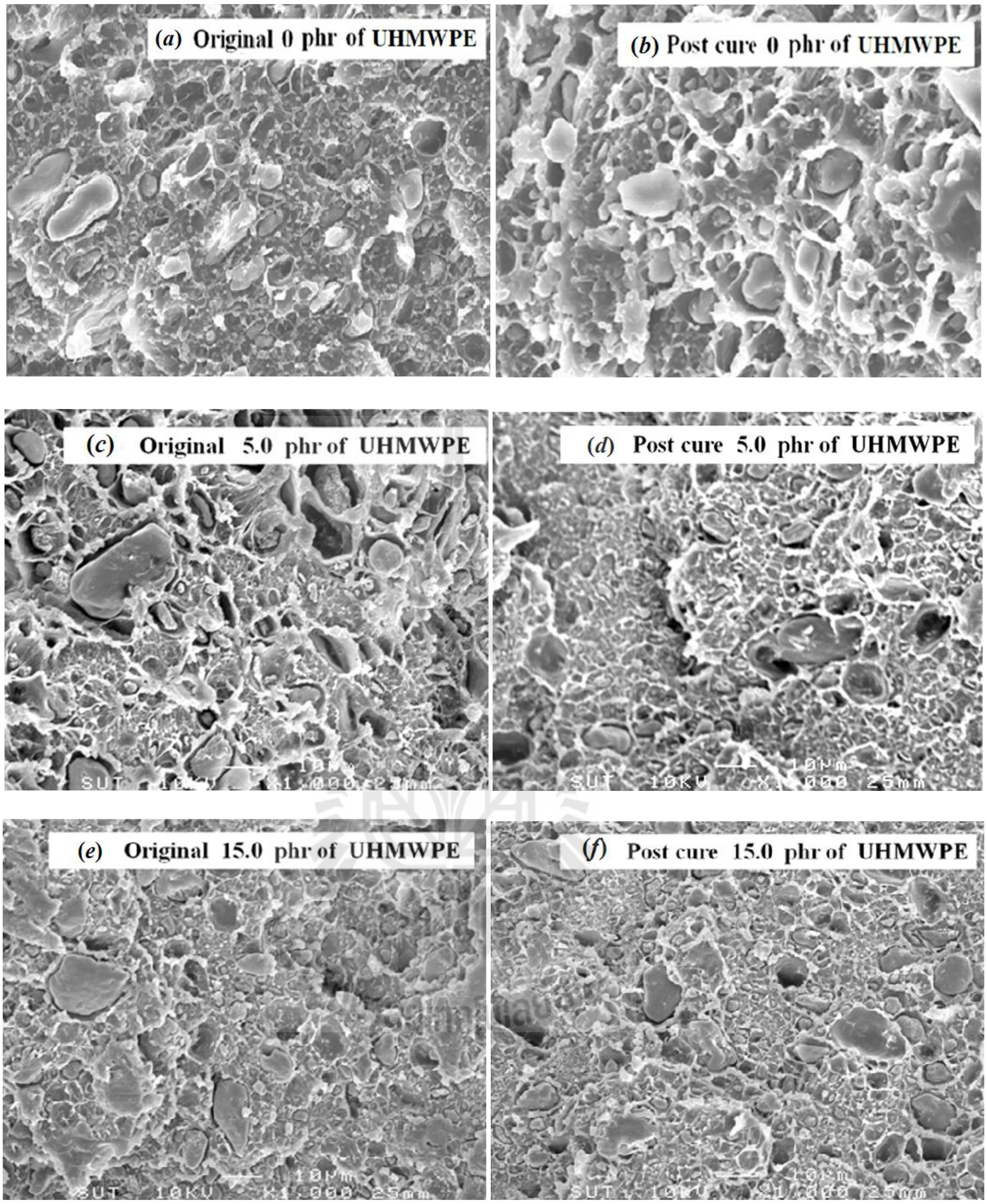


Figure 5.8 Surface characteristics of HDPE/PTFE/UHMWPE blends

5.5.8 Scanning electron microscope of HDPE/PTFE/UHMWPE blends

Figure 5.9 (*a*) to 5.9 (*f*) illustrate the SEM photographs of the notched impact fractured surface specimen for the HDPE/PTFE/UHMWPE blends having the UHMWPE contents varied from 0 to 25, respectively. From the pictures obtained, it confirms that there is no fusion of the PTFE particles. The solid phase is randomly dispersed onto the HDPE/UHMWPE matrix phase. It is also seen poor the adhesion between PTFE and the blend matrix regardless with the UHMWPE contents. Carefully investigation on the fracture traces, it is observed that the interfacial adhesion between the PTFE and the matrix is slightly improved after undergoing the sauna treatment because the gap between the phases is relatively narrower than the sample before treatment. Closer visualizing at the crake traces of the matrix portion, it is seen that there is "**tail-like**" crime seen on the sample with the UHMWPE added. The density of the tail-like is increased with increasing the UHMWPE content. This crake phenomenon would be due to the high toughness UHMWPE added. At this state of discussion, it is conformed that adding the UHMWPE, in the form of UHMWPE/HDPE master batch prepared at 240^{o}C, into the HDPE/PTFE blend, the ultra high molecular weight polymer shows the complete melt blended with the HDPE matrix. According to the SEM observation, the resolved UHMWPE/HDPE blend indicates better fracture toughness than the matrix without UHMWPE. However as discussed earlier, the high melt viscosity of the achieved HDPE/UHMWPE blend would inhibit the dispersion the PTFE particle. Therefore, agglomeration of the particle would be occurred. Balancing between the toughness improvement by adding the UHMWPE and bad dispersion of the PTFE particle, hence incompetency in the interfacial adhesion, the mechanical properties especially impact strengths were not significantly improved as expected. By extraction the information from the SEM determination, it can reconfirm the previous statements explained the diminished in the flexural and tensile properties and the minor increase in the impact strengths of the HDPE/PTFE/UHMWPE blends. The trade-off between toughness improvement of the HDPE/UHMWPE blend matrix, high melt viscosity of the blend matrix and, consequently, poor dispersion and also adhesion between PTFE and the blend matrix must be taken into consideration. General speaking, the negative effect derive from adhesion is dominated over the toughness of the blend matrix especially at the high UHMWPE content.


(a) Original 0 phr of UHMWPE
(b) Post cure 0 phr of UHMWPE
(c) Original 5.0 phr of UHMWPE
(d) Post cure 5.0 phr of UHMWPE
(e) Original 15.0 phr of UHMWPE
(f) Post cure 15.0 phr of UHMWPE
10µm
SUT 10KV X1,000 25mm

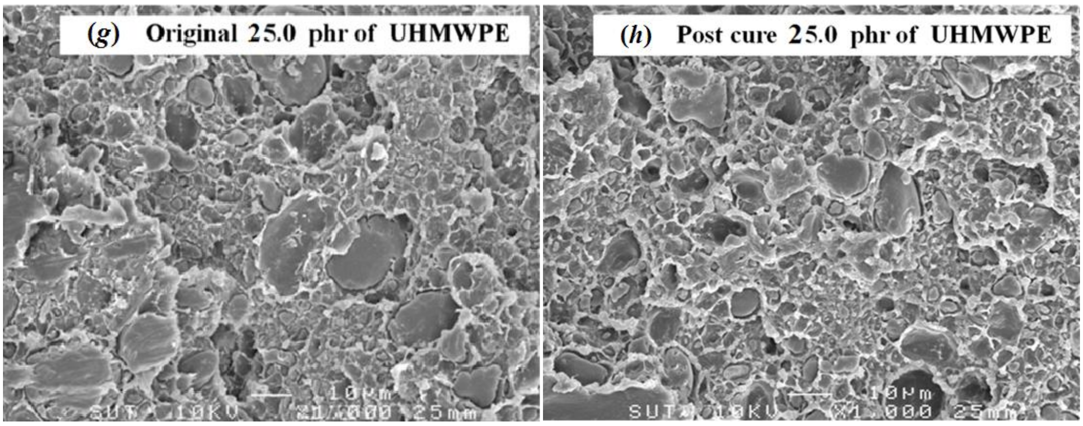


Figure 5.9 SEM micrograph of HDPE/PTFE blend with different concentrations of UHMWPE; (*a*) 0 phr (original) (*b*) 0 phr (cured) (*c*) 5 phr (original) (*d*) 5 phr (cured) (*e*) 15 phr (original) (*f*) 15 phr (cured) (*g*) 25 phr (original) and (*h*) 25 phr (cured), respectively.

5.5.9 Effect of master batching temperatures

From the above section, the ultra high polymer was prepared as master batch at 60 phr of UHMWPE with HDPE at 240^{o}C. Normally, the UHMWPE is difficult to be fused at low temperature. According to the above SEM result, it was seen that the high molecular weight can fused with UHMWPE/HDPE master batch during the mixing process at 190^{o}C. So, it was interested to verify the effect of master batching temperature on the HDPE/UHMWPE blends. The master batching was prepared at screw speed of 10 rpm and the master batching temperature was varied from 200^{o}C, 240^{o}C and 280^{o}C, respectively. Then, the obtained master batches were blended with HDPE at 190^{o}C. The direct blended between HDPE and UHMWPE powder was also obtained for comparison. The compound formulas for HDPE and UHMWPE master batch with silane/DCP crosslink system for the investigation are summarized in Table 5.13. The DCP, silane and UHMWPE contents were kept constant at 1.0, 4.0 phr and 5 phr corresponded with HDPE, respectively. The HDPE in master batch was also counted as the total HDPE in the blend. The performance and characterization of the blends were conducted in normal fashion as described in the above section.

Table 5.13 Compound formula for HDPE/UHMWPE blends

Master batching temp(^{o}C)	Added HDPE(g)	PTFE (g) (phr)	DCP (g) (phr)	Silane (g) (phr)	UHMWPE (g) (phr) (^{o}C)	UHMWPE master batch (g)
Powder form	367	80(20)	4(1)	16(4)	20(5)	53
200	367	80(20)	4(1)	16(4)	20(5)	53
240	367	80(20)	4(1)	16(4)	20(5)	53
280	367	80(20)	4(1)	16(4)	20(5)	53

5.5.9.1 Effect of HDPE/UHMWPE master batching temperatures on MFI

MFI at 200/5.0 of the UHMWPE toughened HDPE/PTFE blends is summarized in Table 5.14 and it is also plotted with the master batching temperatures in Figure 5.10. It is seen that the melt flow index of the blends are independent on the master batching temperature also the direct use as the original powder. It could manifest that the UHMWPE can be perfectly fused HDPE at the given blending temperature, 190^{o}C. Crosslink chain derived from the cooperating silane/DCP crosslink agent during the blending process could generate the shear viscosity and thus providing the shear mixing between HDPE and UHMWPE. For this reason no matter forms of UHMWPE in the blending ingredient, it can be fused with the HDPE matrix. Consequently, the independent of the flow index on the originality of the UHMWPE could be observed. This statement will be further confirmed by the SEM observation later on this section.

Table 5.14 MFI and master batching temperature of UHMWPE

Master batching temp(^{o}C)	**MFI@230/5.00** (g/10min)
Powder form	0.031±0.002
200	0.031±0.003
240	0.032±0.004
280	0.032±0.001

5.5.9.2 Effect of HDPE/UHMWPE master batching temperatures on HDT

The heat distortion temperatures at the standard load of 0.445 MPa of the HDPE/UHMWPE blends are summarized in Table 5.15. The relationship between HDT and the master batching temperature is also graphically presented in Figure 5.10. Again, it is seen that the HDT of the original HDPE/UHMWPE blends are increased when increasing the master batching temperature of UHMWPE from 200 to 280^{o}C. The use of original UHMWPE powder shows the lowest HDT. However, when considering on the sauna cured samples, it is observed that there is the slight decreasing in HDT with increasing the master batching temperatures. Taken the standard deviation into accounting, it could say that the HDT of the sauna cured HDPE/UHMWPE samples are almost constant regardless to the temperatures preparing the HDPE/UHMWPE master batch. By comparison between the refereed material and the HDPE/UHMWPE blends, there is the significant different in HDT for both conditioned specimens. The blends obtained from the master batch are generally shown the higher HDT than the blend derived from the original UHMWPE powder. This difference could be due to the dispersion on the ultra high molar mass chain onto the HDPE matrix. In decent dispersion, direct blending HDPE with UHMWPE powder, would have the lower HDT than the better dispersion. Because of the ultra high polymer chain could act as both toughener and also the fiber-like reinforcing material. Therefore, the HDT of the blends could be increased from the reinforcement effect.

Table 5.15 HDT and master batching temperature of UHMWPE

Master batching temp(^{o}C)	**HDT (oC)**	
	Original	Cured
Powder form	56.7±1.7	63.7±6.1
200	60.1±5.9	70.0±0.4
240	60.7±2.3	69.5±0.5
280	61.2±3.1	68.9±3.1

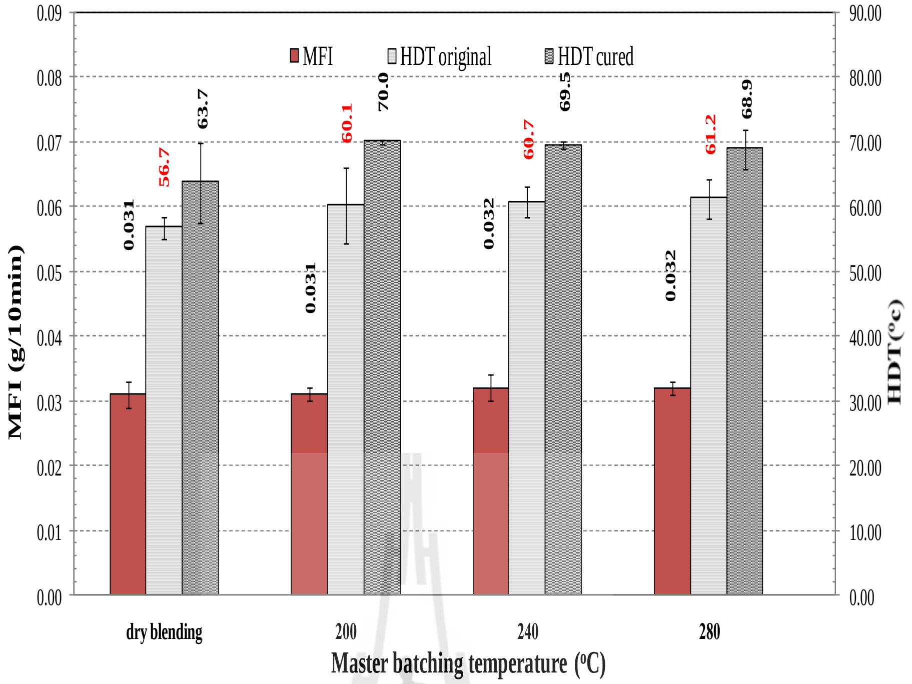


Figure 5.10 MFI and HDT of HDPE/UHMWPE blends and master batching temperatures

5.5.9.3 Effect of HDPE/UHMWPE master batching temperatures on flexural properties

Flexural properties of the HDPE/UHMWPE blends; strength and modulus, tested according to the standard method are given as numerical trend in Table 5.16. They are also presented as the plot with respect to the master batching temperature in Figure 5.11. With the acceptable standard error shown, it is observed that there is no obvious changing in the flexural properties of the blends obtained, regardless to the master batching temperatures, for both original and cured samples. The slightly scattered test results between the HDPE/UHMPE blends could be from the technical errors. It indicated that the previous postulations, dispersion of

UHMWPE and reinforcing effect, cannot have the great effect on the flexural properties of the HDPE/UHMWPE blends. With the decent fusion of the ultra high polymer, small diffusion of the UHMWPE into the HDPE matrix has enough effect on the flexural properties of the blends. Slightly increasing in the flexural strength and modulus of the blends after undergoing sauna incubation could be influenced by the increasing in the crystallinity and crosslink density via the prolong annealing as commonly found throughout this study.

Table 5.16 Flexural properties and master batching temperature of UHMWPE

Master batching temp(^{o}C)	**Flexural strength(MPa)**		**Fluxural modulus (GPa)**	
	Original	Cured	Original	Cured
Powder form	27.84±0.17	28.17±0.26	1.260±0.045	1.280±0.024
200	26.48±0.91	27.70±0.31	1.176±0.065	1.260±0.022
240	27.83±0.60	28.35±0.52	1.304±0.030	1.286±0.044
280	27.28±0.17	27.76±0.32	1.222±0.023	1.262±0.024

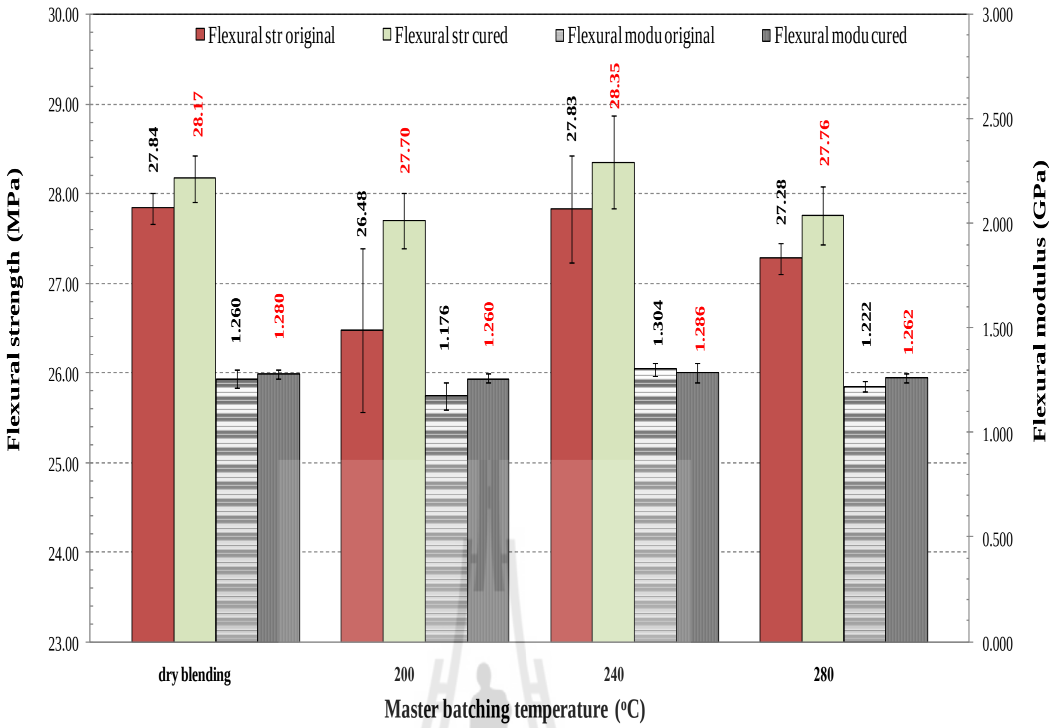


Figure 5.11 Flexural properties and master batching temperature of UHMWPE

5.5.9.4 Effect of HDPE/UHMWPE master batching temperatures on tensile properties

Tensile properties; strength, modulus and % strain at break, of the HDPE/UHMWPE blends using the HDPE/UHMWPE master batch processed at the temperatures from 200°C, 240°C and 280°C are shown in Table 5.17. The plot of the test values in corresponding with the master batching temperature is also illustrated in Figure 5.12. Within the standard deviation, the similar trend found in the tensile properties is observed. There is no obviously differentiation in the strength and modulus except for the % strain at break on the blends obtained from the various UHMWPE forms. The % strain at break shown in Figure 5.13 reviews that the fractional decreasing in the test values with the master batching temperatures is noticed. Typically, the % strain of HDPE is approx. two times higher than the value of UHMWPE. Better dispersion of the UHMWPE into the HDPE matrix would decrease the elongation characteristic of the blends. However, according to the results obtained, the effect is minor. Therefore, taken both strength and modulus of the blends, it could strengthen the above statement that degree of dispersion of UHMWPE and the reinforcing effect cannot have the great effect on the mechanical properties of the HDPE/UHMWPE blends. With the decent fusion of the ultra high polymer, small diffusion of the UHMWPE into the HDPE matrix has enough effect on the flexural properties of the blends. The high melt viscosity of the crosslink chain induced by silane/DCP added can assist the fusion of the UHMWPE into the HDPE matrix nevertheless it is used as the original powder formed. There is no need to master batch the polymer beforehand if only mechanical properties of the blends are needed.

Table 5.17 Tensile properties of HDPE/UHMWPE and master batching temperature of UHMWPE

Master batching temp(°C)	**Tensile strength(MPa)**		**Tensile modulus (GPa)**		**Elongation at break (%)**	
	Original	Cured	Original	Cured	Original	Cured
Dry blending	19.20±0.26	20.07±0.24	0.662±0.024	0.668±0.063	93.69±8.29	91.33±9.79
200	19.37±0.21	19.94±0.13	0.606±0.050	0.596±0.065	89.76±7.74	79.24±5.60
240	19.31±0.21	20.17±0.20	0.614±0.045	0.604±0.058	90.86±6.93	86.32±5.36
280	19.38±0.24	20.04±0.19	0.566±0.027	0.622±0.082	85.09±9.55	80.24±8.74

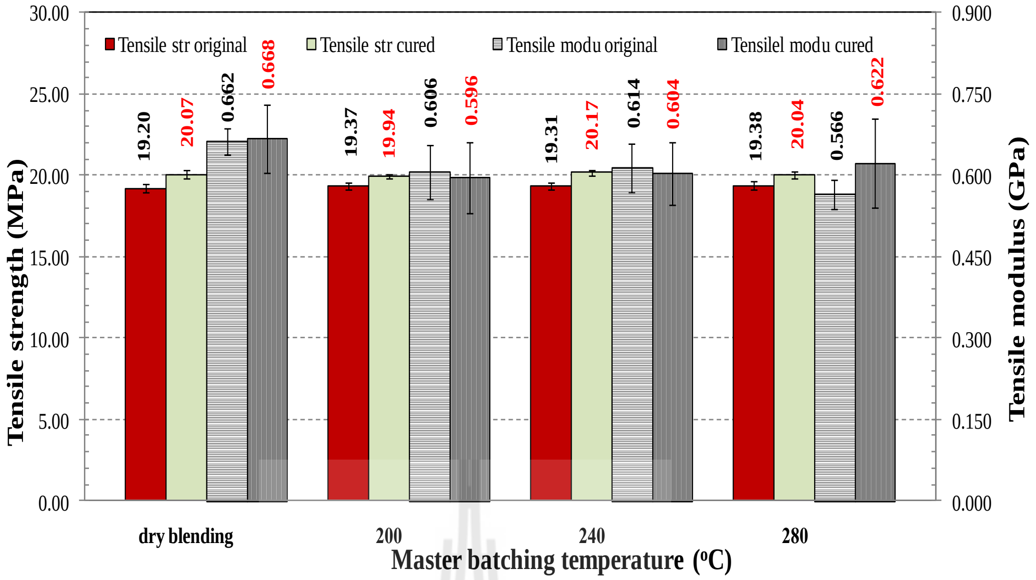


Figure 5.12 Tensile strength and modulus and master batching temperature of UHMWPE

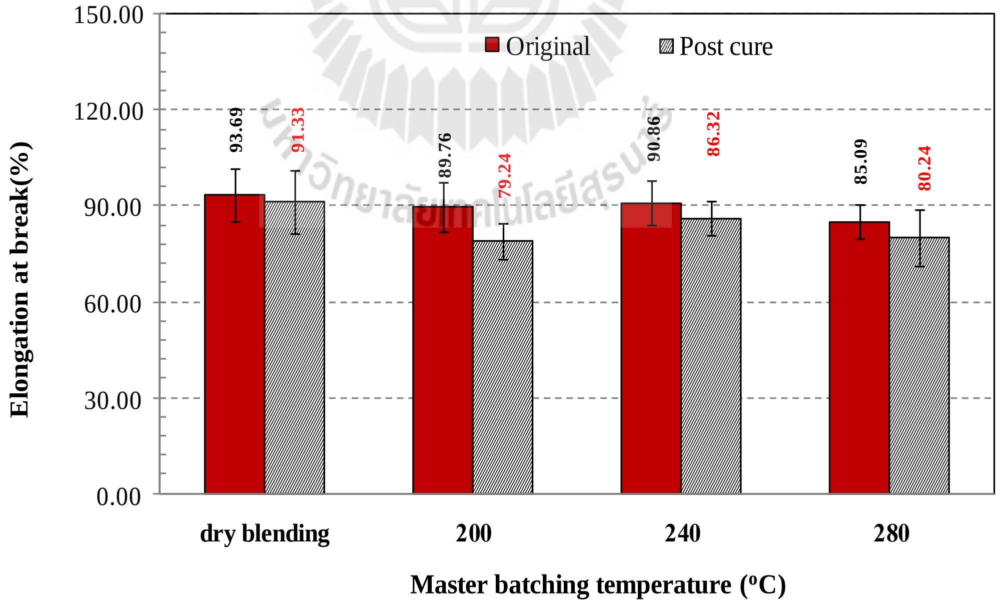


Figure 5.13 % Elongation at break and master batching temperature of UHMWPE

5.5.9.5 Effect of HDPE/UHMWPE master batching temperatures on impact strengths

The fracture toughness of HDPE/UHMWPE blends was obtained as the notched and unnotched impact strengths and their test results conducted on both original and cured samples are summarized in Table 5.18. They are also plotted against the master batching temperatures shown in Figure 5.14. For the unnotched mode of test, all of the specimens were strike under the impact energy of 5.4 kJ. It was resolved that the specimens were not broken at this impact energy. Therefore, the numeric test figures cannot be reported and hereby they are referred as “non break, NB”.

Considering the notched impact figures obtained, it is seen that the very minimal change in the strength with the master batching temperature is observed. Without the ambiguous judgment, it could state that the impact strength of the HDPE/UHMWPE blends are tiny slightly increased with increase the master batching temperatures. Closer observation, taken the sample obtained by direct adding the UHMWPE powder with HDPE and the sample using UHMWPE master batch at 280°C, it is quite obvious seen that the impact strength of the blend derived from master batch is higher than the former one. From the test figures obtained, it is also noticed that the strength of the samples is a little bit higher after undergoing sauna curing process for all blends. The similar trend regarding to the master batching temperature as found in the original one is also evidenced. The better in the impact strength of the HDPE/UHMWPE blend using master batch compare with the one blended with UHMWPE powder is also witness.

Again regarding to the impact strength examination, it can review that the slight improvement of the impact strength of the HDPE/UHMWPE blends with increasing the master batching temperature is might be due to the good melt dispersion of the high molecular weight polymer with the polymer matrix at high master batching temperature. However, excess mixing temperature of the master batch does not have the significant improvement of the blend. In term of the efficiency of blending procedure, the use of master batch pellet would be more efficient than the powder form. By using the single feeder, pre blending the solid particle with vast difference in the size would create would the consistency of the feeding ingredient into the continuous mixer. The tiny particle ingredient, lower bulk density, would be floated on the larger particle, higher in bulk density, during the feeding. Consequently, inconsistency of the blend composition would be experienced. On the other hand, the uneven blend composition would not be occurred when the polymers pellet having the similar in size and bulk density are used. The general conclusion could be made at the stage is that blending of HDPE/UHMWPE using the UHMWPE master batch shows slightly improvement in the notched impact strength without creating the feeding difficulty.

Table 5.18 Impact strength and master batching temperature of UHMWPE

Master batching temp(^{o}C)	**Notched (kJ/m^2)**		**Unnotched (kJ/m^2)**	
	Original	Cured	Original	Cured
Powder form	8.45±0.35	9.26±0.20	NB	NB
200	8.84±0.21	9.75±0.88	NB	NB
240	8.80±0.27	9.97±0.87	NB	NB
280	8.88±0.13	9.74±0.51	NB	NB

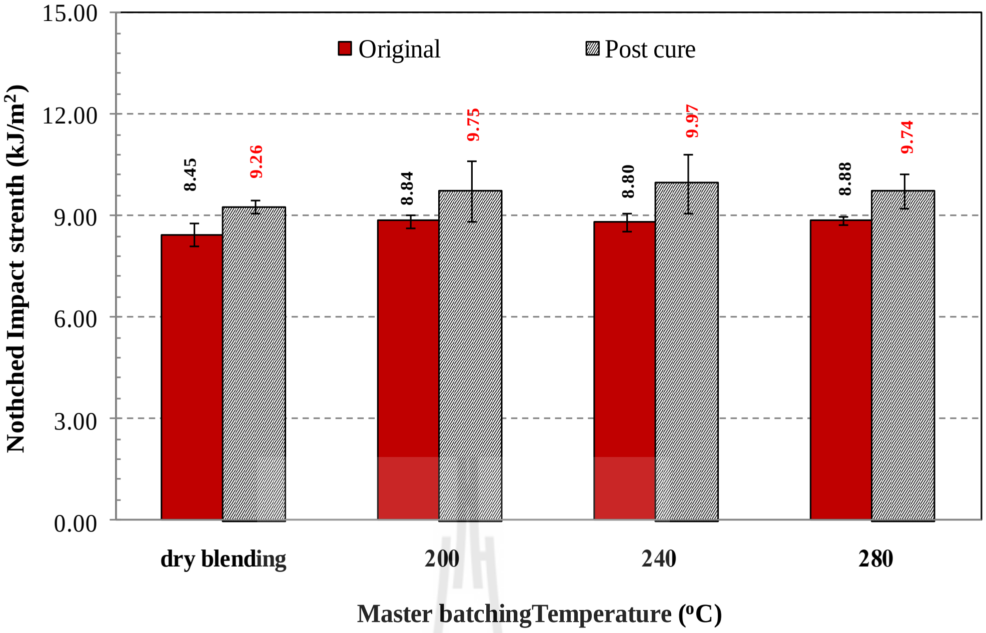


Figure 5.14 Notched impact strength and master batching temperature of UHMWPE

5.5.9.6 Effect of HDPE/UHMWPE master batching temperatures on surface properties

Surface tensions of the blends with the water were adoptedly examined by mean of water drop diameter ratio on the HDPE/UHMWPE film and the referee material, PTFE/glass, D_{sample}/D_{PTFE}. The calculation outcome is given in Table 5.19 and it is presented as the graphical relationship with the master batching temperature in Figure 5.15. Taken the standard deviation for the granted, it would say that the surface tensions of the blend’s film obtained are not depended on the master batching temperature. The calculated ratios found are very tiny changed for all samples. Also, in comparison between original and cured samples, it is seen that there is no different in the ratio after the sauna incubation. It is meant that good blending between HDPE and UHMWPE is obtained regardless to the form of the UHMWPE used. The capillary force effect due to the gaps between disperse phase and matrix phase, bad interracial adhesion, are not resolved in the blends. The ratio, more than 1.0, indicates that the water surface tension of the HDPE/UHMWPE is better than on the PTFE.

Table 5.19 Water drop diameter ratio and master batching temperature of UHMWPE

Master batching temp(^{o}C)	**D_{sample} /D_{PTFE}**	
	Original	Cured
Powder form	1.03±0.06	1.08±0.11
200	1.05±0.10	1.09±0.04
240	1.06±0.05	1.06±0.02
280	1.05±0.05	1.05±0.04

5.5.9.7 Effect of HDPE/UHMWPE master batching temperatures on wear properties

The wear resistance, % weight loss under constant load, of the HDPE/UHMWPE blends is summarized in Table 5.20 and plotted with the temperatures in Figure 5.15, for both original and cured samples, respectively. Apparently, the % weight of the blend is relatively low, less than 0.5%, which is one of the outstanding properties of the polyethylene based materials. In comparison between the test values of HDPE/UHMWPE blend obtained using the UHMWPE powder form and using the master batch form, the test figures show that the former has less wear resistance, higher in % weight loss, than the later one. However, when judging the effect of master batching temperatures, it is seen that the abrasion resistance by mean of the %.weight loss do not depend on the temperatures because the constant % weight loss is observed. With the given master batching temperature, it is also noticed that sauna incubation does improve the wear resistance of the blends. This is two folds explanation. One is due to the increase in the surface hardness via the increasing the crystallinity during the prolong annealing process. The later is the good interfacial adhesion between lower abrasion resistance HDPE and higher abrasion resistance UHMWPE. Hence, the better battle for surface corrosion due to the friction rupture is resolved.

Table 5.20 % weight loss and master batching temperature of UHMWPE

Master batching temp(^{o}C)	**Weight loss (%)**	
	Original	Cured
Powder form	0.42±0.06	0.41±0.10
200	0.40±0.08	0.37±0.14
240	0.40±0.12	0.38±0.13
280	0.40±0.27	0.37±0.16

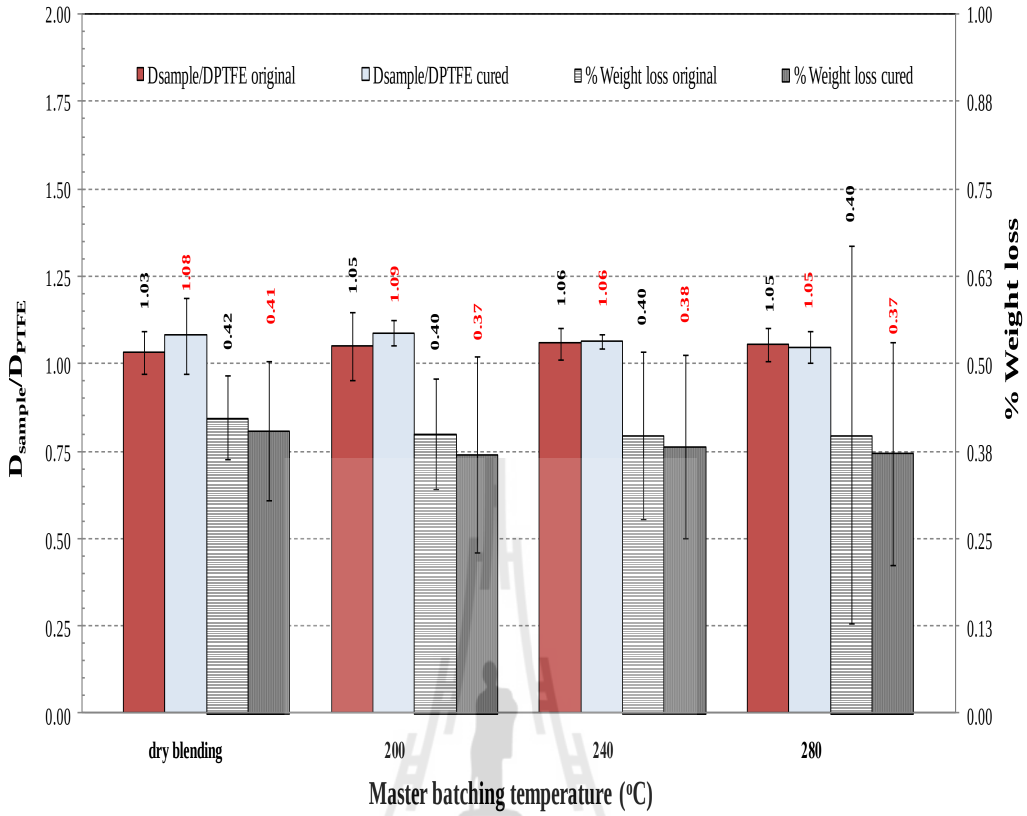


Figure 5.15 Surface properties and master batching temperature of UHMWPE

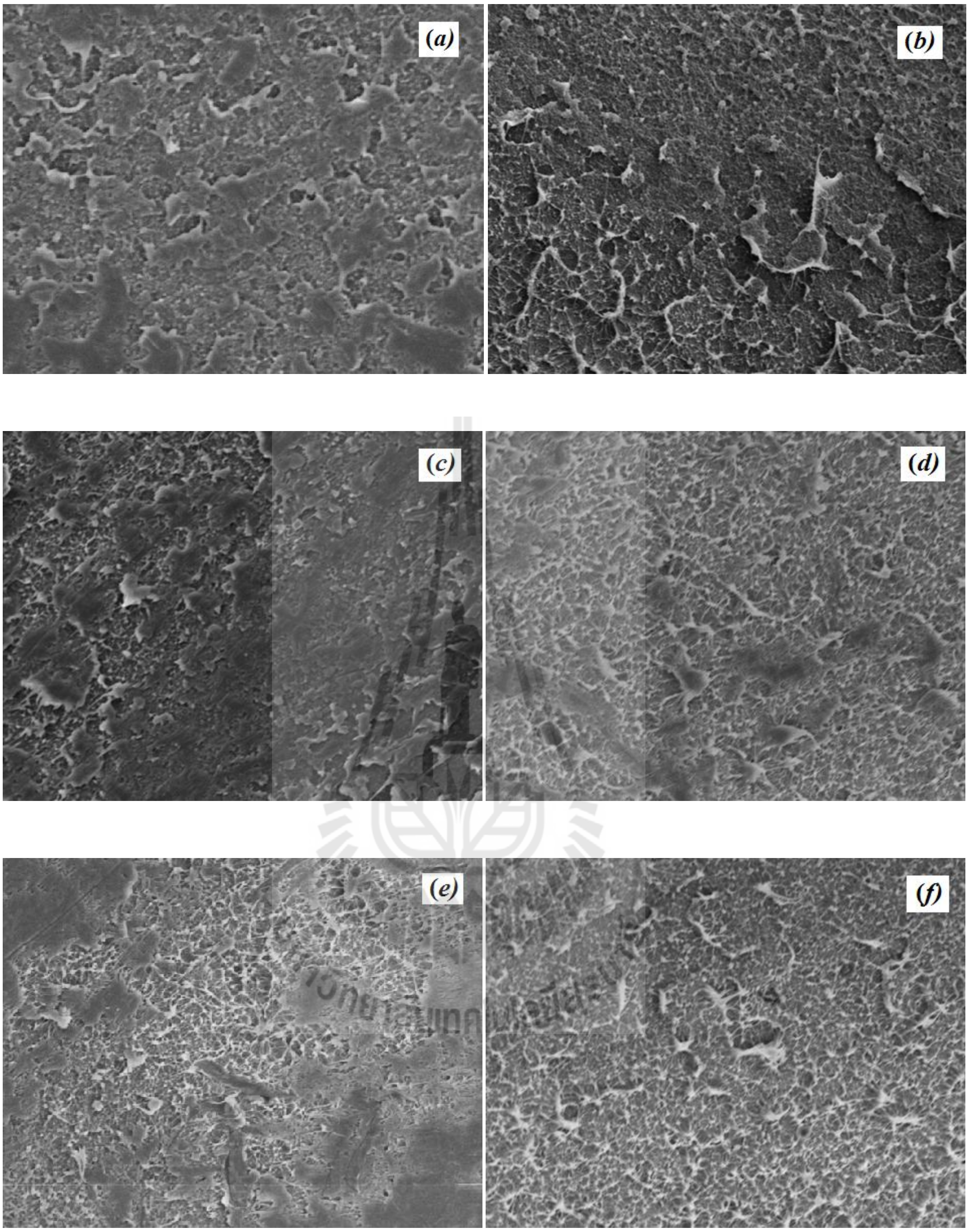
5.5.9.8 SEM visualization

From the above performance properties discussion, efficiency of fusion and good blending between HDPE matrix and UHMWPE toughener were hypothesis for the variation of the test figures. Therefore, the SEM evidence would be merit to be the final verdict for the discussion in this research study. SEM photographs of the impact fractured surface of all the above HDPE/UHMWPE blends are examined and illustrated in Figure 5.16 (***a***) to 5.16 (***h***), respectively. According to the photographs shown, the uneven crack scenes are resolved from the UHMWPE toughening effect. Therefore, the dispersion of the molecular weight polymer on the

HDPE matrix can be observed from these traces. It is obviously seen that the distribution of UHMWPE in the matrices phase is better at the blend using the higher temperature master batching especially at 280°C. It indicates that good dispersion and mixing is obtained when blending HDPE with the master batch manufactured at higher temperature. Decent dispersion, but not good enough, is observed on the blend using the original form, powder, of UHMWPE. However, regarding to the SEM pictures, it is seen that the UHMWPE can be fused with the HDPE matrix regardless to the originality of use.

It is difficult to verify the effect of the sauna curing on the fractured surface of the given HDPE/UHMWPE blend. But with the carefully visualization on the SEM result, it could notice that the length of the fiber like fracture traces of UHMWPE is longer after the sample was treated in the sauna oven. As conclude in the impact strength discussion, the toughness of the cured sample was improved after undergoing the moisture treatment.

According to SEM examination obtained, it can manifest that better dispersion of UHMWPE was obtained by blending HDPE with UHMWPE by using UHMWPE/HDPE master batch pellet. UHMWPE can be fused with HDPE matrix phase by direct blending between the high molecular weight polymer powders but relatively poor dispersion would be achieved. Consequently, incompetency in the toughness would be experienced. There is no significant effect of the UHMWPE/HDPE master batching temperatures on dispersion and then the properties of the HDPE/UHMWPE blend.


(a)
(b)
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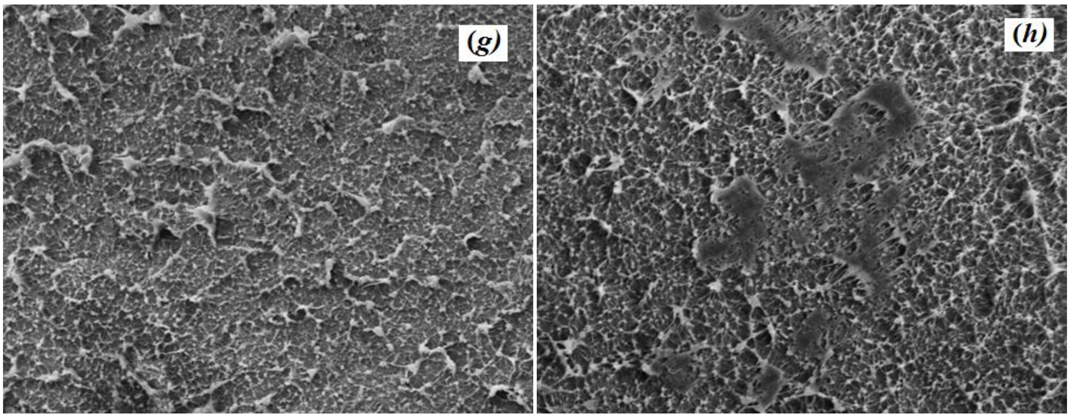

Figure 5.16 SEM micrograph of HDPE/UHMWPE blend with different master batching temperature; (*a*) Dry blending (original) (*b*) Dry blending (cured) (*c*) 200^{o}C (original) (*d*) 200^{o}C (cured) (*e*) 240^{o}C (original) (*f*) 240^{o}C (cured) (*g*) 280^{o}C (original) and (*h*) 280^{o}C (cured) at X1000, respectively.

5.6 Conclusion

The UHMWPE was added into the HDPE/PTFE blend as toughener in order to improve the impact and also flexural properties of the blend. The results showed that at higher UHMWPE content, above 5 phr with respect to the HDPE matrix, the mechanical properties especially flexural and tensile were decreased with increasing the UHMWPE contents. However, the impact strength was increased with increasing the UHMWPE addition. The increasing in the melt viscosity by adding the UHMWPE and hence retarding the melt mixing for the added ingredient was taken into explanation for the diminishing in the flexural and tensile properties and minor increase in the impact strengths of the HDPE/PTFE/UHMWPE blends. The trade-off between toughness improvements of the HDPE/UHMWPE blend matrix, high melt viscosity of the blend matrix and, consequently, poor dispersion and insufficient adhesion between PTFE and the blend matrix must be taken into consideration for the blending purpose. General speaking, the negative effect derived from adhesion was dominated over the toughness of the blend matrix especially at the high UHMWPE content.

The ability for the added UHMWPE powder to be fused with HDPE matrix was clarified. The effect of HDPE/UHMWPE master batching temperatures was resolved. It was manifested that better dispersion of UHMWPE was obtained by blending HDPE with UHMWPE by using UHMWPE/HDPE master batch pellet. UHMWPE was fused with HDPE matrix phase by direct powder blending but relatively poor dispersion was observed. Consequently, incompetency in the toughness would be occurred. The final properties of the HDPE/UHMWPE blends using the HDPE/UHMWPE master batch form concluded that there was no significant effect of the UHMWPE/HDPE master batching temperatures at 200°C, 240°C and 280°C. The fusion and also dispersion of the UHMWPE within the HDPE matrix in the final blends were relatively similar. Consequently, there were no major differences in the properties of the HDPE/UHMWPE blend.

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CHAPTER VI

EFFECT OF FILLERS ON THE CROSSLINKED HDPE/PTFE/UHMWPE BLENDS

6.1 Abstract

HDPE/PTFE/UHMWPE composite filled with fire clay and binary filler; fire clay/talc, were studied. The twin screw compounded was injected into test specimen. It was fond that the MFI of the fire clay filled HDPE/PTFE/UHMWPE composite was increased, lower in the melt viscosity of the composite. Fire clay filler acted as the lubricator type of filler. The mechanical and thermal properties of the composite material were slightly increased with increasing the fire clay loading. However, the fracture toughness of the composite material was deceased. The adhesion between the filler and polymer matrix was taken for the explanation. For HDPE/PTFE/UHMWPE composite filled with fire clay/talc fillers, it was found that the flow index of the composite did not increased by increasing the fire clay fraction. It was also found that the fire clay filler did not have the significant effect on the HDT of the composite. Moreover, the mechanical properties by mean of tensile and flexural were also slightly inferior when high portion of fire clay was added. The impact toughness was slightly increased with increasing the fire clay ratio. The surface properties both wear and tension were not obviously affected by the fire clay filler. The larger particle size of the fire clay than the talc was taken into explanation.

In the peeling force investigation on the surface of the blends, it was evidenced that the lower peeling force was obtained while adding low polarity fillers, 30/20 talc and fire clay, onto the crosslinked HDPE/PTFE/UHMWPE. The easiness for removing the rubber crepe from the surface was equated to the low surface tension of PTFE. The smoothness surface due to the lower molding shrinkage and low polarity of the fillers were taken into explanation.

6.2 Introduction

The fillers are important roles to modify the properties of polymers and beneficial in reducing the unit cost of the material. In general polymer industries; packaging materials, household, automotive parts, there are many type of fillers used including calcium carbonate, carbon black, and talc. They have generally been used to enhance the mechanical properties of polymers. The adding of filler has direct effect to characteristic of polymer compound such as increasing in the density and the modulus of elasticity as well as in the compressive and flexural, the tensile and shear strength, impact strength, hardness, heat deflection temperature and heat resistance. Some of fillers added would influence the process ability of the compound. Normally, reducing in the melt viscosity, increasing the flow ability during processing, is found by incorporating small amount of filler. The opposite effect would be resolved when the fiber like filler is added at the above critical concentration. Moreover, the filler would benefit the ease of surface deflect and also enlighten the surface finish.

Recall from previous chapter, it was found that blending of UHMWPE with HDPE at high content had negative effect to mechanical properties of the HDPE/PTFE/UHMWPE blends. The increasing in the melt viscosity of the blend was main drawback when adding UHMWPE. As the above introduction, the filler addition is one of the typical compounding methods to enlighten the polymer compound toughness. In this report chapter, the commercial talc filler and the powder derived from the fire clay waste was employed as the fillers to investigate their influence on the flow ability, mechanical and also surface properties of the blend compound. The minimal amount of UHMWPE, at 5 phr, is used for the blend materials. It was prepared as HDPE/UHMWPE master batch at 240°C.

6.3 Research methodology

6.3.1 Materials and chemical reagents

High density polyethylene (HDPE, EL-Lene H5814J), is the general purpose high density polyethylene resin that suitable for injection molding process. It was used as the main polymer matrix. This processing graded HDPE has good flow ability and design for high productivity with good toughness product. It is available from SCG-Chemical Co., Ltd. The property of the HDPE matrix used, supplied by the manufacturer, is summarized in Table 6.1.

Table 6.1 Properties of HDPE, EL-Lene H5814J

Properties	Test Method	Value, Unit(SI)
Melting Temperature	ASTM D2117	131^{o}C
Melt Flow Index	ASTM D1238@190/2.16	14 g/10min
Notched Izod Impact	ASTM D256	2 kJ/m^2
Tensile Strength at Yield	ASTM D638@50 mm/min	27.5 MPa
Elongation at Break	ASTM D638@50 mm/min	620%
Flexural Modulus	ASTM D790	1225 MPa
Heat Deflection Temperature	ASTM D648@0.455 MPa	75^{o}C

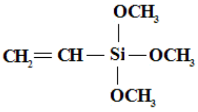
PTFE white powder, Zonyl® MP 1300 fluoroadditive, is a free flowing grade. It is designed for using as an additive in other materials to impart low surface energy and other fluoro polymer attributions. It is available from DuPont®. It was employed as dispersed phase. According to the manufacturer data sheet, the powder has the average particle size of 12 μm. Other properties of the powder, provided by the supplier, are summarized in Table 6.2.

Table 6.2 Properties of Poly(tetrafluoroethylene), Zonyl® MP 1300.

Properties	Test Method	Value, Unit
Melting Temperature	ASTM D4894	325±5^{0}C
Particle Size Distribution	Laser Microtrac	12 μm
Specific Surface Area	Nitrogen Adsorption	1.5 - 3.0 m^2/g
Average Bulk Density	ASTM D4894	0.425 kg/l

Low viscosity and water clear liquid vinyltrimethoxy silane (VTMS), commercialized as Silquest® A 171, was used as crosslink system in conjunction with peroxide via the moisture incubation or sauna treatment. The chemical structure and physical properties of the liquid silane is given in Table 6.3. The chemical was directly used without further dilution and purification and dilution.

Table 6.3 Properties of VTMS, Silquest® A171

Properties	**Value, Unit**
Chemical structure	 $CH_2=CH-Si(OCH_3)_3$
Boiling point	122°C
Specific gravity, 25°C	0.967 g/ml

Low melting temperature, <50°C, solid dicumyl peroxide (DCP) flake was employed as free radical generator. It is a commercial grad and available throughout the rubber chemicals suppliers. The chemical formula of this peroxide is shown in Figure 6.1. Again, it was used without further purification. It has low melting point, slightly above 50°C. It is normally decomposed and generated quit stable free radical at the temperature above 120°C.

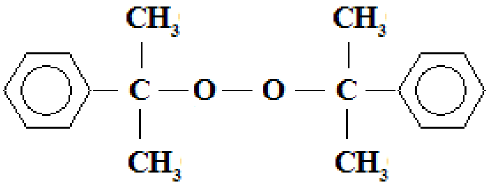


Figure 6.1 Chemical structure of dicumyl peroxide ($C_{18}H_{22}O_2$)

The talc filler, Jetfine® 3CA, with average particle size of 1.3 μm, is supplied from Luzenac. The physical properties of the particular fillers used provided by the manufacturer are summarized in Table 6.4.

Table 6.4 Physical properties of Talc, Jetfine® 3CA

Physical Properties	**Value, Unit(SI)**
Particle size	1.2-1.4 μm
Density	2.78 g/cm^3
Specific surface area	14.5 m^2/g
Chemical Composition	SiO_2(61%), MgO(32%), Al_2O_3(0.3%), Fe_2O_3(0.2%) and CaO(0.9%)
Decomposition temperature	900-1000 ^{o}C

Fine powder of Asahi Kasei Sunfine ultrahigh molecular weight polyethylene (UHMWPE), UH 900, is added into HDPE compound in the form of HDPE/UHMWPE master batch to enhance the toughness and also the surface properties. The properties of the powder, provided by the supplier, are presented in

Table 6.5. It was used as the master batch form with HDPE. The UHMWPE at 60 phr with respect to the HDPE was master batched at 240^{o}C as described in the previous chapter.

Table 6.5 Properties of UHMWPE (UH900)

Properties	**Test Method**	**Value, Unit(SI)**
Melting temperature	DSC method	136^{o}C
Melt density	JIS K 7112	940 kg/m^3
Izod Impact	JIS K 7111	None folding
Tensile Strength at Yield	JIS K 7161	24 MPa
Elongation at Break	JIS K 7161	330%
Flexural Modulus	JIS K 7171	1100 MPa
Heat deflection temperature	JIS K 7191	85^{o}C

Fire clay (K35) of Siam refractory industry is a normal mud, simple as that, but a mud with higher Alumina (AL) content. Has usually whiter-lighter color. Its melting starts at 1600 Celsius °C or 2912 Fahrenheit °F point. Only special manufacturing technologies of those expensive materials change their properties and usage applications. The physical properties of fire clay are summarized in Table 6.6.

Table 6.6 Physical properties of Fire clay (K35)

Physical Properties	**Value , Unit(SI)**
Type	High duty fire clay
Melting Temperature	1600°C
Particle size	>50 μm
Density	2.0-2.2 g/cm^3
Porosity	16-26%
Color	Cream yellow
Chemical Composition	Al_2O_3(34%), SiO_2(50%), Fe_2O_3 CaO MgO K_2O Na_2O TiO_2 (6-27%)

6.3.2 Material preparation

6.3.2.1 Pretreated PTFE

The PTFE was pretreated with silane/DCP as batch wise process in the internal mixer. The calculated amount, with respected to 100 g of PTFE powder, of 0.5 phr of DCP was dissolved in 1 phr of silane. The clear solution was promptly added into the PTFE powder in the mixing chamber equipped with the roller rotors. The dry blending was performed at 100°C and rotors speed of 80 rpm for 5 minutes. The treated powder was emptied and stored in tightly closed container at least overnight.

6.3.2.2 Preparation of HDPE/UHMWPE master batch

The master batch of HDPE and UHMWPE was prepared at 60 phr of UHMWPE with respect to HDPE by melt mixing in co-rotating twin screw extruder. It was done in order to ease the feeding difficulty and also reducing the fusion temperature of the high molecular weight polymer during compound process at low temperature. The master batch processing was carried out at screw speed of 10 rpm and the barrel temperature of 240^{o}C for all zones. The well melt mixing HDPE/UHMWPE strand was pelletized into polymer pellet. It was used as toughener in the blend. The exact amount of UHMWPE in the blend was diluted from the concentrate master batch.

6.3.2.3 Preparation of fire clay

Fire clay particle size was reduced in by grinding with ball mill. The Fire clay and the ceramic ball with the diameter 0.5, 1.0 and 2.0 cm were added into ceramic cylinder with ¾ by volume of the mixing blow. It was grid for 15 minutes, after that, the fine powder was sieved through the 50 µm standard mesh. It means that particle size of the fire clay power less than 50µm was obtained and used in this research study. Before mixing with HDPE, the fire clay was vacuum dries at 80^{o}C for 2 hours to eliminate the residual moisture.

6.3.3 Compounding procedure

In this chapter, the further improvement properties of HDPE/PTFE compounds, especially flow ability, is also one the main interest objectives. There were two attempts regarding to the improvement properties of the HDPE/PTFE compounds by using the designed fillers; (i) addition only fire clay (ii) adding the combined fillers between talc and fire clay. It is known that adding the particulate filler into the polymer at decent concentration not only preventing the volume shrinkage injected product but also enhance the flow ability of the melt. Because the round shape filler would ease the flow resistance by rolling movement effect.

6.3.3.1 Using fire clay as filler

HDPE was pre dried in the vacuum oven at 80^{o}C for 2 hours. The water clear solution of the 1 phr of DCP and 4 phr of silane was prepared. Then, it was vigorously mixed with the dried HDPE pellet. The exact amount of solid ingredient; fire clay, treated PTFE and UHMWPE master batch pellet, were added into the HDPE and completely well mixed. The solid mixture was immediately fed via the single screw feeder into intermeshing co-rotating twin screw extruder having the screw diameter of 25 mm, L/D ratio of 20 and consisted of three quadrate kneader disk. The compounding processing was performed at screw speed of 10 rpm at the constantly barrel temperature at 190^{o}C for all 4 zones. The compounded strand was pelletized.

6.3.3.2 Using talc and fire clay as fillers

Fire clay and talc powder were dehumanization at 80^{o}C for 2 hr in the vacuum oven. The melt mixing procedure between talc/fire clay fillers, PTFE and the HDPE were achieved in the same manner as describe in section 6.3.3.1. The typical binary fillers concentration existed in the HDPE/PTFE/UHMWPE blends was 50 phr. The ratios between talc and fire clay were varied from 40:10 to 10:40 with respect to 100 g of HDPE matrix. Compounding with only talc and fire clay only was also obtained.

The typical melt mixing procedures between the fire clay and combined fillers with HDPE conducted in this research work as described above is schematically summarized in Figure 6.2.

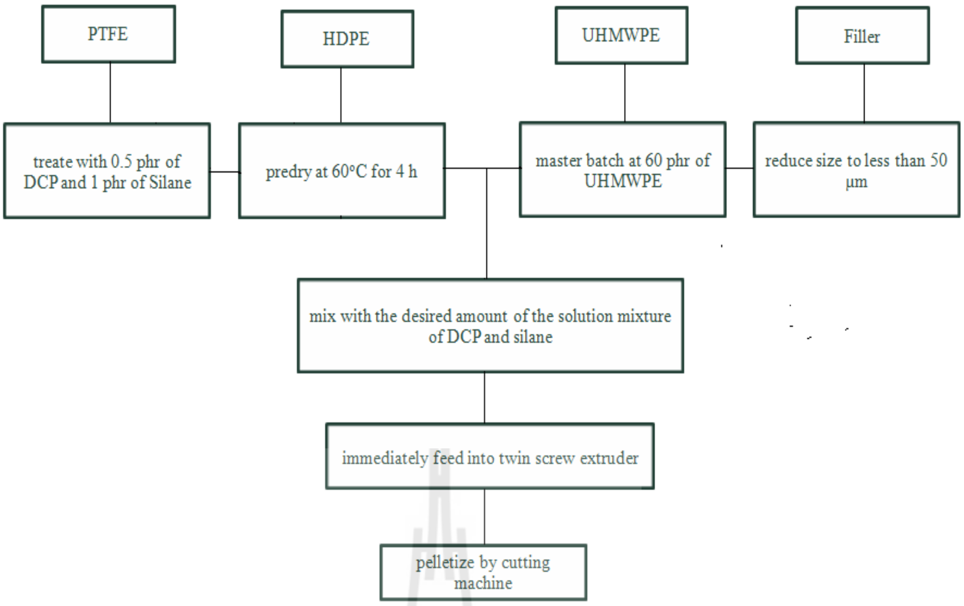


Figure 6.2 Process chart for the HDPE/PTFE/UHMWPE/Filler compounding

6.3.4 Test Specimen Preparation

6.3.4.1 Specimen for mechanical testing

The tensile, flexural and impact testing samples were obtained by injection molding using a reciprocating screw injection molding machine, CHUAN LIH FA T80. The barrel temperatures profile for molding was 190, 200, 210 and 220^{o}C from feed to nozzle zones, respectively. The family and artificially balanced two plate mold consisted of two dumb bells, type I and type IV, one rectangular bars for flexural and HDT testing and one short rectangular bar for impact testing with standardized dimension was employed. The size and shape of the injected specimens were in accordance with ASTM regulations. The temperature of mold cooling water was carefully controlled at 30^{o}C. The injection pressure was electronically controlled at 80% of the maximum machine capacity. The injected samples obtained were divided into 2 sets. The first one was allowed to anneal at room temperature overnight and it was categorized as “**original**” sample. The later was undergone post curing in the sauna oven saturated with moisture at 65^{o}C for at least 12 hours. The incubation temperature was far above the T_g of HDPE. Therefore, the moisture molecule could be freely penetrated into the polymer chains. These specimens were classified as sauna cured or shortly as “**cured**” sample.

6.3.4.2 Thick film preparation

Thick film samples for the abrasion examination were manufactured by hot compression process. The compound pellet was placed in between two PTFE/Glass woven sheets. The sample was transferred into the plat molds. The mold was preheated at 200^{o}C for 10 min then slowly pressed at 110 MPa at 200^{o}C and the pressure was constantly retrained for 6 min. The pressed film was immediately removed and allowed to cool down at room temperature. The smooth film with the approximate thickness of 0.4 mm was obtained. The abrasion test specimen was scissor cut into the rounded shape with the diameter of 4.5 cm. The centered hole was punched using hole puncher. The sheet sample was also divided into 2 categories, original and sauna cured, respectively.

6.3.4.3 Peel test specimen

The test substrates, the assigned polymer sample, were obtained from the injection molded piece. The square box shape with the dimension of 10X10 cm and the part thickness of 1.5 mm was injection molded in the similar machine setting as for preparing the previous test specimen. Except for the PTFE referee, the thin PTFE/Fiber Glass pieces were directly cut from the commercial fabric and used as it is. The thin rectangular polymer sample, 10X2.5 cm (L x W), was cut by using the razor sharp and edges trimmed by sand paper. The commercial adhesive tape was applied onto the smooth surface of the injected polymer substrate. The peeling samples were placed into the vacuum bagging for hours to ensure that good surface adhesion between the substrate and adherent, and also removing the air bubble between the surfaces.

For the preparation of the polymer substrates and dried natural rubber crepe, the identical rectangular samples as used in the above adhesive peeling test were placed onto the shallow container. The fresh cut natural rubber latex was filled into the container. The latex was allowed to dry by moisture evaporation under the sunlight for at least two weeks. Eventually, the samples were thoroughly coated by the moisture depleted rubber crepe. It was gentry cut and disassembled from the container. They were, again, transferred into vacuum bag and evacuated in the hot oven at 80^{o}C for at least three hours in order to remove the excess moisture and also get rid of the air voids between the rubber and the compound test piece. By performed in this manner, the dried rubber crepe was adhered on the polymer substrate and ready for the peel test.

6.4 Properties Measurement

6.4.1 Rheological testing

The rheological property, melt flow index (MFI), was examined. The MFI of the HDPE/PTFE/UHMWPE/Filler pellet was tested at 230/5.0 in accordance with ASTM D 1238 using the Kayeness melt flow indexer. The obtained pellet samples were vacuum dried in the oven at 80°C for at least 2 hours to eliminate the possible moisture residual. Testing samples was allowed to completely molten at

230^{o}C for 240 seconds and it was driven through the capillary die (Ø 1 mm.) using piston load of 5.0 kg. Three cuts were performed at the cut times of 30 second. The extrudate was weighed and calculated into the melt flow index value in the standard unit of g/10min.

6.4.2 Physical properties assessment

6.4.2.1 Impact strengths

Impact strengths of the HDPE/PTFE/UHMWPE/Filler(s) were tested in according with ASTM D 256 in the Izod mode. The injection molded specimen obtained with the dimension of 12x50x3 mm. was notched using the notching machine. The identical injected samples were tested without notching. Notched and unnotched impact strengths were conducted at room temperature using the impact pendulum with impact energy of 2.7 Joule for the notched and 5.4 Joule for the unnotched samples, respectively. The impact values were reported as impact strength, kJ/m^2, that were calculated from impact energy required for completely breaking the sample over the cross section area at fractured area. At least five samples were tested for each polymer compound and the average values were obtained and reported.

6.4.2.2 Flexural properties

Flexural properties by mean of the strength and modulus of the HDPE/PTFE/UHMWPE/Filler(s) sample were examined in accordance with ASTM D790. The injection molded sample with the dimension of 12x120x3.5 was used for the test. Instron universal testing machine, model 5565, with the load cell of 5 KN and three point bending test fixture with span length of 56 mm, 16 times of the thickness of the test specimen, was employed. The crosshead speed of 50 mm/min was constantly controlled. The test specimen was placed plat wise to the bending load. The test was conducted at room temperature in normal atmospheric condition. The flexural strength and modulus were computerized using the following equation (6.1) and (6.2), respectively.

$$\textbf{Flexural Strength} = \frac{3PL}{2[bd]^2} \quad (6.1)$$

Where: P = load at a given point on the load-deflection curve (N)
L = support span (mm)
b = width of beam tested (mm)
d = depth of beam tested (mm)

$$\textbf{Flexural Modulus} = \frac{L^3 m}{4(bd)^3} \quad (6.2)$$

Where: L = support span (mm)
b = width of beam tested (mm)
d = depth of beam tested (mm)
m = slope of the tangent to the initial straight line portion of the load-deflection curve (N/mm) of deflection.

6.4.2.3 Heat deflection temperature

Heat deflection temperature (HDT) of the HDPE compound was conducted with the ASTM D 648. The sample was tested in the edgewise position, with the support span length of 100 mm. The simple beam with the standard load applied at its center to give maximum stress of 0.455 MPa or 66 psi was followed. The testing machine from Atlas, model HDV 1, was employed. The raising temperature at a uniform rate of 2±0.2^{o}C/min was assigned. Liquid silicone oil was used as heating transfer media. The HDT value was reported in degree Celsius (^{o}C) as soon as the specimen had been deflected to 0.25 mm or 0.01 inch that was monitored by the dial gauge. This temperature was recorded as the deflection temperature under the assigned standard flexural load of the test specimen. Three samples were examined and the average value was reported.

6.4.2.4 Tensile properties

Tensile properties of HDPE composites were examined using the Instron Universal Testing machine, model 5565, with a load cell of 5 kN, crosshead speed of 50 mm/min and a gauge length of 80 mm. Tensile tests were performed according to ASTM D 638. The dimension of the molded dumbbell shaped specimens with 12.7 mm in width at narrow section, 20 mm in overall width, 80 mm in gauge length, 165 mm in overall length and approx. 3.5 mm in thickness was used for performing the test. Five samples were tested in each HDPE/PTFE/UHMWPE/Filler(s) sample. Calculated tensile strength (N/m^2 or Pa) was given by dividing the maximum load, in Newton force (N), by the average original cross sectional area in the gage length segment of the specimen in square metres (m^2). Calculated modulus of elasticity was performed by extending the initial linear portion of the load extension curve and dividing the difference in stress corresponding to any segment of section on this straight line by the corresponding difference in strain. Calculated percent elongation at break was computed by reading the extension at the fracture point and then dividing that extension by the original gage length and multiplies by 100.

6.4.3 Surface properties investigation

6.4.3.1 Wear test

Wear ability of the HDPE/PTFE/UHMWPE/Filer(s) composites by mean of abrasion testing was investigated. The standard method, ASTM D 4060 Abrasive Wear Testing, was followed. It is the measurement of the weight loss under the specified test conditions. In this study, specimens were abraded for 500 rounds of rotation under the constant load at 0.25 kg and H-18 abrader type. The weight loss of the sample was computed as the below relationship. Three circular film specimens prepared by the procedure describe in section 6.3.4.2 was engaged. Each of specimens was individually tested. The averaged the weight loss was gathered and presented.

$$\textbf{\%Weight loss} = [\,\frac{\text{Weight before test} - \text{Weight after test}}{\text{Weight Before test}} \text{ x } 100 \qquad (6.3)$$

6.4.3.2 Surface tension observation

The surface tension of the polymer sample, either on film or injected specimen, is normally tested by liquid drop angle measurement using the appropriate test liquid and laser equipped machine. At the presence time, such expensive equipment is not available in our research laboratory. Attempting to investigate the surface tension of the HDPE/PTFE/UHMWPE/Filler(s) material was conducted by using the adaptive, or comparative, test method. The deionized water was used as the test liquid. The adopted method to evaluate the surface tension of the test liquid on the surface of the injected or film specimen was constructed. The micro pipette with the minimal volume capacity of 20 μl equipped with the micro tip adapter was used for applying the water drop. Drops of 1.0 μl of the deionized water through the micropipette were carefully placed onto the cloth dried surface of the polymer sample. The diameter of the water drop (D_{sample}) was measured through the optical micro scope and digitally analyzed. The diameter of the water drop on the commercial PTFE/Glass woven sheet (D_{PTFE}) was obtained in the exact fashion and used as referee values. It was assumed that D_{PTFE} was resolved from the surface tension of water on pure surface of PTFE film. Then, the ratio between the diameters of the drop on the sample divided by the drop on the standard PTFE sheet was computed according to the equation 6.4. If the computed number is higher than 1.0, it means that the diameter of demonized water on the HDPE/PTFE/UHMWPE/Filler(s) sample is larger than on the PTFE. It indicates that the surface tension of the sample is higher than the surface tension of PTFE. Vice versa, if the ratio less than 1.0 is obtained, it reviews that the surface tension of the polymer compound is lower than the referee PTFE sheet. Consequently, low surface tension material, the liquid unlikely to be adhering or spread on the material surface, will be concluded.

$$D_{Sample}/D_{PTFE} \quad \frac{\text{Diameter of drop on sample}}{\text{Diameter of drop on the standard PTFE sheet}} \tag{6.4}$$

6.4.3.3 Peel testing

Peel strength testing is adopted in accordance of ASTM D903 to evaluate the force of surface adhesion between polymer sample and natural rubber crepe and also the adhesive tape. Instron universal testing machine, model 5565, with load cell of 10 N was employed. Average load per unit width of bond line required separating progressively one member from the other over the adhered surface at separation angle of approximately 180^{o} and separation rate of 152 mm/min was controlled. The test was conducted at room temperature in normal atmospheric condition. Manually separation of the free end of the adherent from the surface of the sample for a distance of about 20 mm was manipulated. The peel test specimen was placed in the testing machine by clamping the free end of the adherent on the top grip and clamping the end of polymer sample on the bottom grip. The adherent member was striped from the specimen approximately at an angle of 180°. The total separation for a peel distance of 140 mm was assigned. The actual peeling or stripping length and force was computerized recorded. Then, the average striping force value for every 4 mm was manually calculated. The plot between the average forces with the peeling distance was constructed. The peeling load was indicated, in Newton force, by averaging the upper constant force between the given peeling distances as demonstrated in Figure 6.3

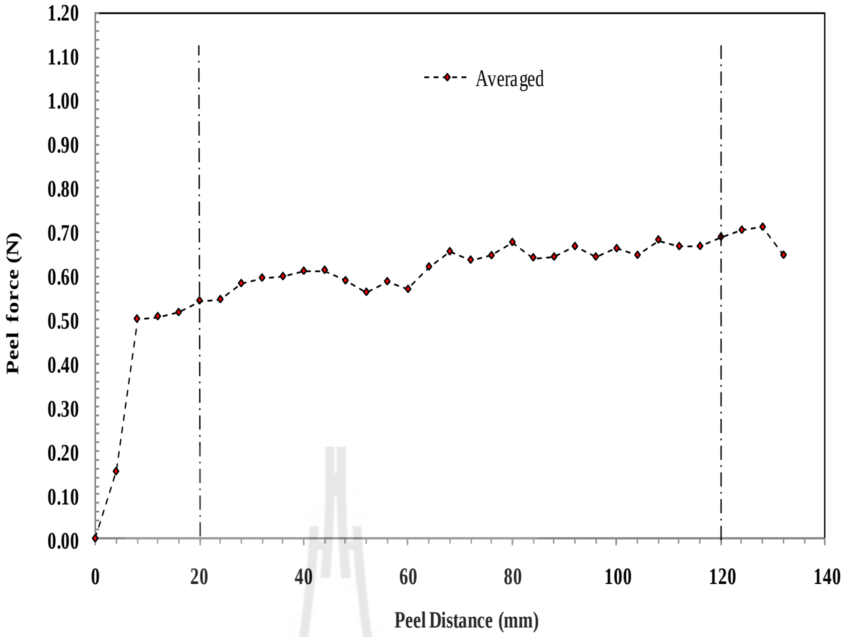


Figure 6.3 The obtained plot from peeling test

In this study, the injected bars of the polymer sample were employed for the test except for the PTFE/Glass referee where the thin sheet which the exact aerial dimension was cut from the roll. In case of using commercial adhesive as adherent, the tape was adhere on the test specimen polymer and firmly pressed. The specimen was transferred into vacuum bag and then vacuum bagging for ten minutes at room temperature to remove the possible air bubble on the interfacial surface. For the natural rubber crepe sample, the freshly rubber latex was poured onto the polymer sample bars and let it dried in the opened air for 2 week. The excess rubber edges were trimmed. Then, they were transfer into the oven at 80°C for 3 hours to ensure the completely dried was obtained. The rubber crepe specimen was then vacuum bagging in the identical manner as the adhesive preparation.

6.4.4 Morphological investigation

Morphology of the fractured surface of HDPE/PTFE/UHMWPE and HDPE/PTFE/UHMWPE/Filler(s) sample obtained from the notched impact testing was used to investigate using scanning electron microscope (SEM). The broken piece of specimen was cut in to small piece to fit the SEM sample holder. It was securely attached onto the sample holder. The samples were coated with layers of gold for 8 minutes by ionization before analysis. SEM photograph was taken using JOEL machine model JSM6400 at the typical accelerating voltage of 10 keV.

6.5 Results and discussions

6.5.1 HDPE/PTFE/UHMWPE filled with fire clay

According to the blending formula of HDPE/PTFE/UHMWPE with increasing the fire clay contents are shown in Table 6.8. The fire clay content was varied from 0 to 50 phr (Composite FC#0, Composite FC#10, Composite FC#20, Composite FC#30, Composite FC#40 and Composite FC#50) in order to find out its effect on the properties of the blends. The PTFE, silane, DCP and UHMWPE were constantly kept at 20, 4, 1 and 5 phr respectively for all formula. The amount of HDPE in the master batch formula was computed and then summed to the added virgin HDPE resulted in the total amount of HDPE matrix in the blend ingredient. The HDPE/PTFE/UHMWPE blend without fire clay was used for the sake of reference material. The standard test results of the blends in corresponding with the filler addition are being discussed.

Table 6.8 The blend formula of HDPE/PTFE/UHMWPE filled with fire clay

Sample	HDPE(g)	PTFE (g) (phr)	DCP (g) (phr)	Silane (g) (phr)	UHMWPE (g) (phr)	Fire clay (g) (phr)
Composite(FC#0)	367	80(20)	4(1)	16(4)	20(5)	-
Composite(FC#10)	367	80(20)	4(1)	16(4)	20(5)	40(10)
Composite(FC#20)	367	80(20)	4(1)	16(4)	20(5)	80(20)
Composite(FC#30)	367	80(20)	4(1)	16(4)	20(5)	120(30)
Composite(FC#40)	367	80(20)	4(1)	16(4)	20(5)	160(40)
Composite(FC#50)	367	80(20)	4(1)	16(4)	20(5)	200(50)

6.5.1.1 MFI of the fire clay filled blends

The melt flow index, obtained at 230/5.0, of the HDPE/PTFE/UHMWPE filled with 0, 10, 20, 30, 40 and 50 phr of fire clay are summarized in Table 6.9 and it is also graphically shown with respect to the filler content in Figure 6.4. It is obviously seen that, MFI of the blend is increased with increasing the fire clay powder content. It confirmed the above hypothesis that increasing amount of the rounded mineral fire clay filler can enhance the flow stability of the polymer compound. So, the reducing in the melt viscosity will be benefit for the fabrication process especially the injection molding. Not only the shape effect of the filler that increase the flow ability of the blend compound but also the increasing in the crosslinking spaces due to the occupying of the filler particle. The crosslink bridges of the chain would be longer when there are solid particles lies into the free volume. The loosely crosslink, longer bridging, would ease the flow resistance. Therefore, the viscosity of the melt would be decreased. However, when considering the numerical figures of the MFI at 230/5.0 resulted, they are relatively low, high melt viscosity, when compare with the typical injection molding grade polymer. In fact, this type of compound is suitable for the extrusion based process rather than injection ones.

Table 6.9 MFI of HDPE/PTFE/UHMWPE and Fire clay contents

Sample	**MFI@230/5.00**
	(g/10min)
Composite(FC# 0)	0.031±0.003
Composite(FC#10)	0.032±0.001
Composite(FC#20)	0.045±0.005
Composite(FC#30)	0.065±0.002
Composite(FC#40)	0.088±0.006
Composite(FC#50)	0.103±0.003

6.5.1.2 HDT of the fire clay filled blends

The heat distortion temperature was measured at the standard load of 0.445 MPa. The HDT of HDPE/PTFE/UHMWPE filled with various amount of fire clay is summarized in Table 6.10 and it is also graphically shown with respect to the filler content in Figure 6.4. As expected, it is seen that the HDT of both original and cured samples are increased with increasing the fire clay loading. It is also observed that, at the given fire clay loading, the HDT of the sample is further higher when it was treated in the sauna oven. Form the test results, it reviews that the fire clay filler has the common effect to the polymer compound as typically found in the other mineral fillers. Incorporating the mineral filler into the polymer would typically enhance the thermal property of the material because the particulate filler would act as the deformation reinforcement to environmental heat. Further treatment process via the sauna incubation would probably lead to the increasing in both crosslink density and also the interfacial adhesion between the filler particles and polymer matrix, via the mechanical interlock and chemical bonding. The prolong thermal annealing would typically responsible for the increasing in the crystallinity of the polymers and hence higher the HDT of the sauna cured compound sample.

Table 6.10 Heat deflection temperature of HDPE/PTFE/UHMWPE/Fire clay composites

Sample	**HDT (^{0}C)**	
	Original	Cured
Composite(FC# 0)	62.80±2.55	77.90±1.79
Composite(FC#10)	64.30±0.58	78.90±2.23
Composite(FC#20)	67.60±0.40	79.80±0.60
Composite(FC#30)	70.80±0.20	81.80±0.60
Composite(FC#40)	72.10±0.31	82.90±0.64
Composite(FC#50)	73.80±0.40	83.80±1.37

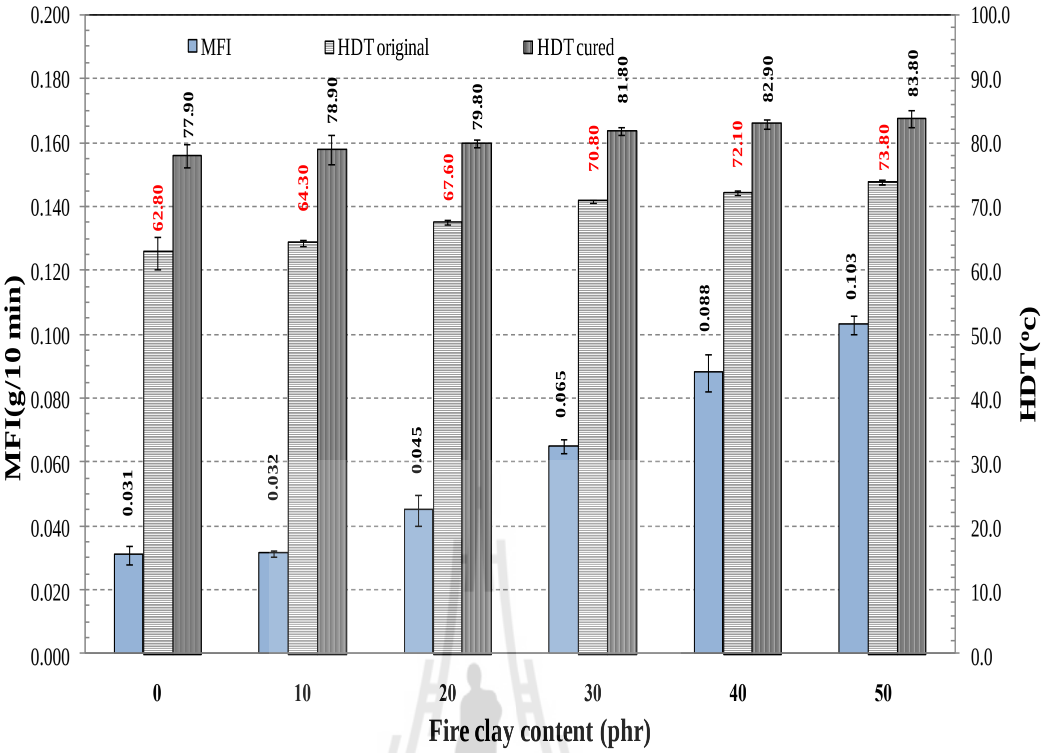


Figure 6.4 MFI and HDT of the HDPE/PTFE/UHMWPE/Fire clay composites

6.5.1.3 Flexural properties of the fire clay filled blends

The flexural properties of the polymer compound filled with mineral filler normally stiffer but brittle when the mineral loading is increased. The flexural properties of HDPE/PTFE/UHMWPE filled with fire clay reported as strength and its modulus are summarized in Table 6.11. They are plotted with respect to the given fire clay concentration in Figure 6.5. It is observed that the flexural strength of both with and without sauna curing samples is linearly increased with increasing the content of fire clay filler. Similarly, flexural modulus of the blend is also increased with increasing the fire clay content. The increasing in both flexural strength and the modulus enlighten that the material shows superior resistance to the bending load. The enhancement of the blending toughness of the blend has two folds explanation. One might be explained by energy dissipation through the filler particle during crack propagation. The more particulate filler type added the more in the energy distribution, less energy intensity, during the material breaking phenomena. Consequently, the crack propagation is retarded. In the same time, the bending strength of the material is increased. The mentioned positive effect would be dominantly observed when the interfacial between added filler and the matrix is superior. The opposite result with respect to the increasing the mineral filler loading would be found when the micro voids resolving form the dislike interfacial adhesion between filler and matrix of the compound are formed. According to this study outcome, it manifest that the good interfacial adhesion between fire clay and HDPE blend matrix is retrained.

When comparing between original and cured sample at the given fire clay loading, it is seen that the strength and modulus of the sauna cured specimen are further improved. The assisting of prolong annealing at the high temperature of the blends would introduce the mechanical interlock and chemical bonding between filler particles and matrix phase via the silane/moisture crosslink reaction. Hence, the flexural properties of the blends would be greater.

According to the flexural properties obtained in this section, the conclusion in the term of the toughening effectiveness of the fire clay added into the HDPE/PTFE/UHMWPE blends could be written. The bending strength of the blends was enhanced by adding the fire clay filler.

Table 6.11 Flexural properties of HDPE/PTFE/UHMWPE/Fire clay composites

Sample	**Flexural strength(MPa)**		**Fluxuralmodulus(GPa)**	
	Original	Cured	Original	Cured
Composite(FC# 0)	25.59±1.27	29.98±1.17	1.252±0.082	1.470±0.086
Composite(FC#10)	28.72±0.58	31.11±0.59	1.376±0.009	1.512±0.059
Composite(FC#20)	31.99±0.35	33.92±0.33	1.594±0.054	1.682±0.032
Composite(FC#30)	35.65±1.77	36.88±0.41	1.846±0.119	1.878±0.051
Composite(FC#40)	37.74±0.11	40.09±0.82	2.020±0.037	2.108±0.056
Composite(FC#50)	40.75±0.77	42.41±0.44	2.214±0.057	2.310±0.070

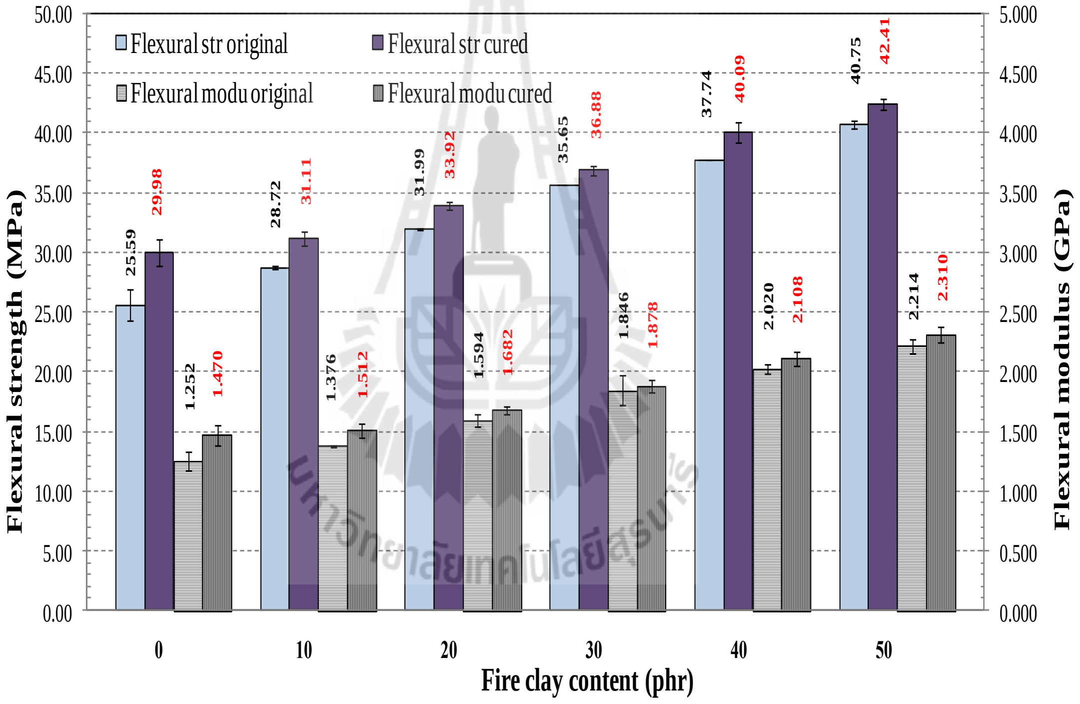


Figure 6.5 Flexural properties of the HDPE/PTFE/UHMWPE filled with fire clay

6.5.1.4 Tensile properties of the fire clay filled blends

Tensile properties; strength, modulus and % elongation at break, of the HDPE/PTFE/UHMWPE/Fire clay composite obtained at strain rate of 50 mm/min are shown in Table 6.12. Mean while, Figure 6.6 is the plot between the strength and modulus with the given fire clay loading in the composite material. According to the test values found, it is seen that strength and modulus are almost linearly increased with increasing the fire clay addition. Also, it is typically noticed that the strength and modulus of the sauna cured are higher than the original one, especially at low filler concentration.

In Figure 6.7 shows the relationship between % elongations at break and fire clay contained in the HDPE/PTFE/UHMWPE blends. In contradiction with the strength and modulus, it reveals that the % elongation of the compound is vastly decreased with increasing the fire clay loading. It also notices that the elongation at break of the sauna treated specimen is generally lower than the original one. Regarding to the % elongation at break, it indicates that the tension flexibility of the composite material is decreased with increasing the filler used. This is quite typical for the polymer compound characteristic.

The slowly increasing in the strength and modulus but suddenly decreasing in the elongation of the fire clay filled material manifests that the tension toughness of the material is inferior when the amount of the mineral filler added into blend matrix is increased. Increasing in the crosslink density via the sauna induced condensation between silane and moisture molecule is lower the tension toughness of the derived composite. It is also the common symptom for the filler filled polymer compound where the loosing of the flexibility of the material is experienced by adding the particulate mineral filler. The adhesion and the crosslink density, as explained in the above flexural properties section, are taken into account for the effect of the fire clay filler on the tensile properties. For the sake of polymeric material industry, the trading off between cost reduction and, sometimes, processing ability of the material and incompetence of the mechanical properties must be greatly but carefully considered.

Table 6.12 Tensile properties of HDPE/PTFE/UHMWPE/Fire clay composites

Sample	**Tensile strength(MPa)**		**Tensile modulus (GPa)**		**Elongation at break (%)**	
	Original	Cured	Original	Cured	Original	Cured
Composite(FC# 0)	16.44±0.19	18.02±0.16	0.680±0.030	0.702±0.051	55.89±0.33	52.22±0.34
Composite(FC#10)	16.77±0.41	18.05±0.45	0.686±0.040	0.722±0.049	21.31±4.00	20.09±2.66
Composite(FC#20)	17.38±0.09	18.38±0.13	0.756±0.053	0.812±0.024	16.27±1.41	14.39±1.33
Composite(FC#30)	18.39±0.68	19.37±0.39	0.830±0.102	0.884±0.116	9.85±0.63	11.04±0.93
Composite(FC#40)	19.28±0.54	19.63±0.32	1.042±0.083	1.064±0.072	7.70±0.68	8.79±1.29
Composite(FC#50)	20.72±0.87	20.79±0.76	1.085±0.042	1.142±0.097	7.65±0.09	6.56±1.26

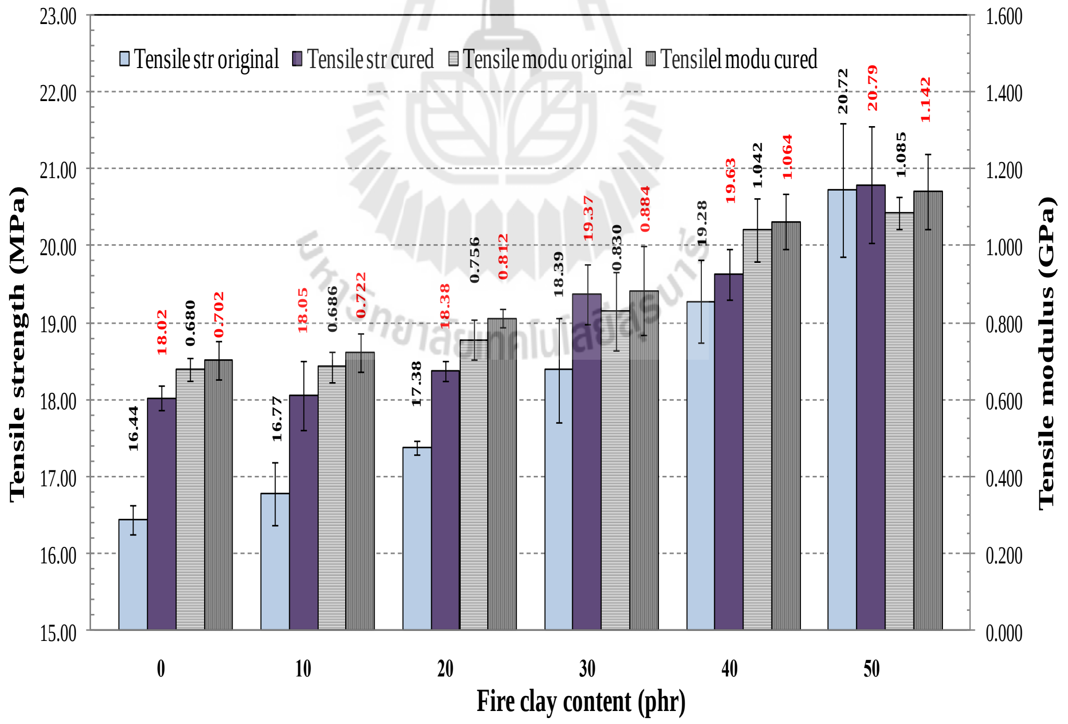


Figure 6.6 Tensile properties of HDPE/PTFE/UHMWPE/Fire clay composites

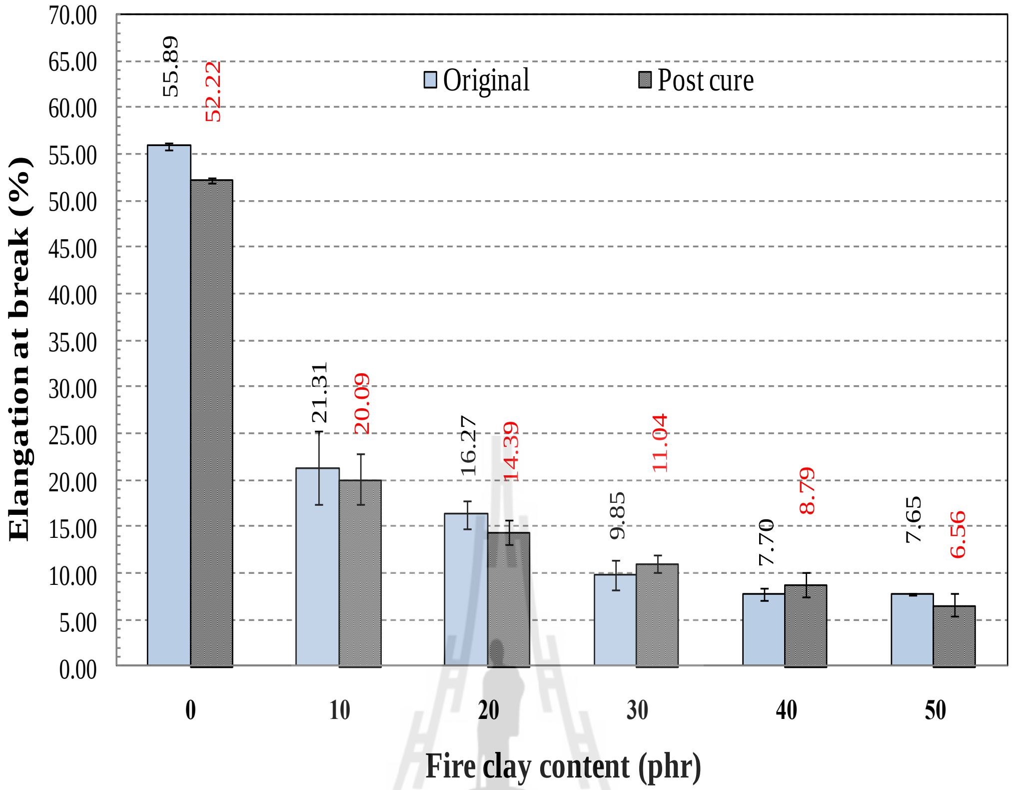


Figure 6.7 Elongation at break of HDPE/PTFE/UHMWPE/Fire clay composites

6.5.1.5 Impact strength of the fire clay filled blends

The fracture toughness of HDPE/PTFE/UHMWPE blend with fire clay content was obtained as impact strengths, notched and unnotched modes of test, for both original and cured samples. It was found that within the impact pendulum at 5.4 kJ it was unable to perform the test for the unnotched samples. All the unnotched specimen were non breakable. For the testing on the notched samples, the test outcomes are summarized in Table 6.13 and they are plotted against the fire clay concentration shown in Figure 6.8.

According to the result shown, it is observed that the notched impact strength of both original and cured HDPE/PTFE/UHMWPE filled with fire clay filler is obviously decreased when increasing in the fire clay content. It is typical phenomenon for the solid filled polymer compound where the toughness of the material is normally decreased with increasing the filler contents especially when the adhesion between the filler and polymer matrix is poor. The brittle material would be indentified. Ambiguously, generally the sauna incubation would increase the network density of the blend matrix and hence lower the toughness of the composite material. However, from the notched impact figures, it is noticed that the impact strength of the sauna cured samples are generally increased after the treatment. This positive effect would be due to the increasing in adhesion between fire clay particles and HDPE/PTFE/UHMWPE matrix phase via sauna treatment.

Table 6.13 Impact strengths of HDPE/PTFE/UHMWPE/Fire clay composite

Sample	**Notched (kJ/m^2)**	
	Original	Cured
Composite(FC# 0)	6.27±0.21	7.86±0.13
Composite(FC#10)	6.25±0.37	7.81±0.21
Composite(FC#20)	6.02±0.17	6.36±0.11
Composite(FC#30)	5.95±0.48	5.92±0.20
Composite(FC#40)	4.66±0.16	5.09±0.21
Composite(FC#50)	4.31±0.15	4.49±0.14

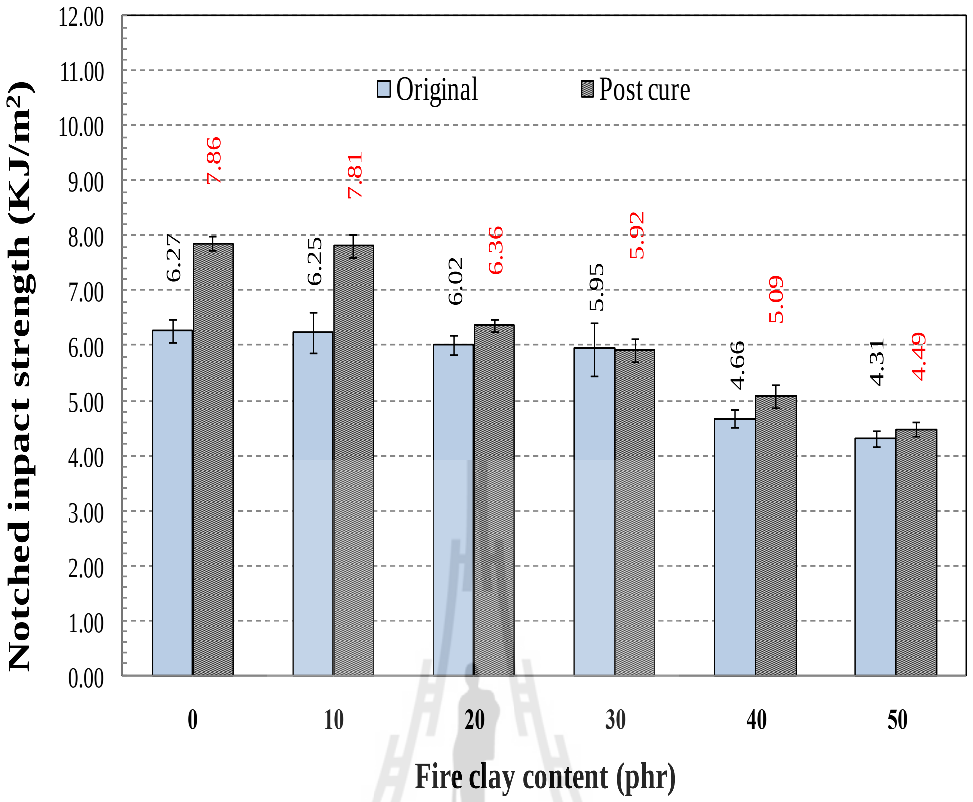


Figure 6.8 Notched impact strength of HDPE/PTFE/UHMWPE/Fire clay composite

6.5.1.6 Surface properties and fire clay contents

The diameter of water drop ratio to indentify the surface tension of HDPE/PTFE/UHMWPE filled fire clay filler for the original and cured samples are gathered in Table 6.14 and also plotted with the filler content in Figure 6.9. It is found that the figures obtained from the original specimens are slightly decreased with increasing the fire clay loading. The ratios are less than 1.0 at the fire clay loading above 10 phr. On the other hand, the calculated ratio is almost unchanged for the sauna cured specimen. But all the calculated ratios are less than 1.0.

As specified throughout this research work that the figure less than 1.0 in the water drops ratio between sample and the referee material, PTFE, indicate low surface tension of the sample obtained. Within the result found, it could say that the fire clay filler lower the surface tension of the HDPE/PTFE/UHMWPE composite especially when the loading is above 10 phr. It manifests that the fire clay filler is might be hydrophobic in nature. Therefore, adding the filler into the polymer blend matrix can influence the surface properties of the composite outcome.

Table 6.14 Water drop diameter of HDPE/PTFE/UHMWPE/Fire clay composites

Sample	**D_{sample} /D_{PTFE}**	
	Original	Cured
Composite(FC# 0)	1.03±0.07	0.99±0.01
Composite(FC#10)	1.03±0.02	0.99±0.02
Composite(FC#20)	0.96±0.04	0.99±0.04
Composite(FC#30)	0.94±0.04	0.99±0.03
Composite(FC#40)	0.93±0.03	0.99±0.03
Composite(FC#50)	0.89±0.06	0.98±0.04

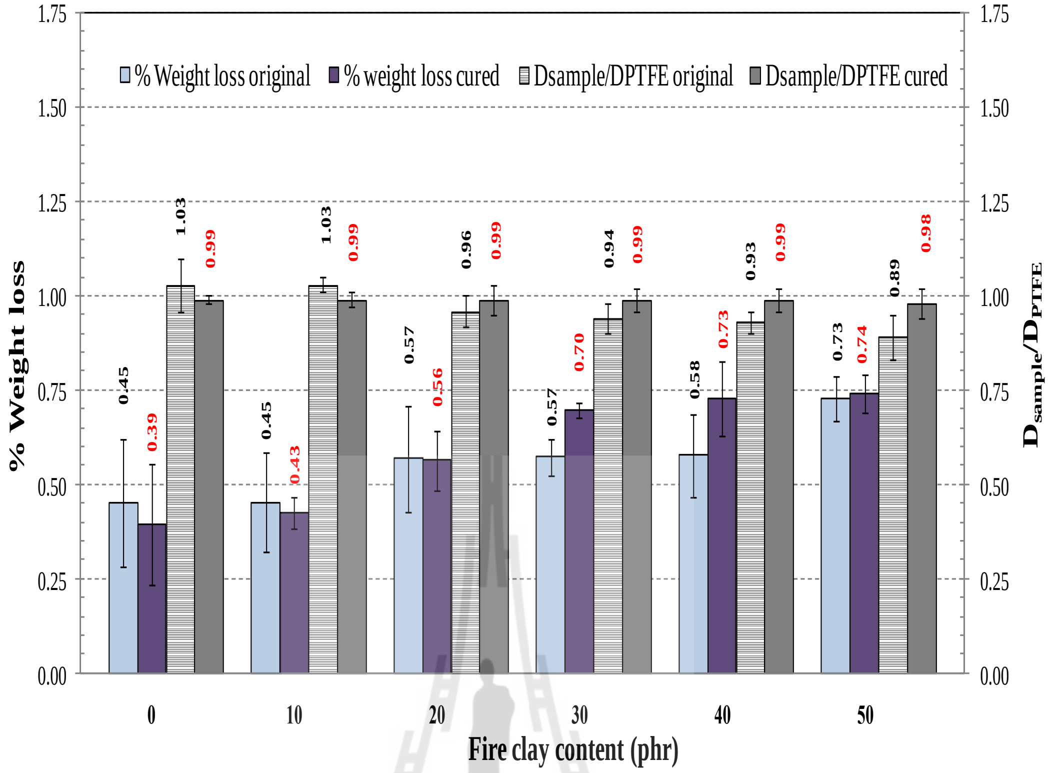


Figure 6.9 Abrasive resistances of HDPE/PTFE/UHMWPE/Fire clay composites

6.5.1.7 Wear resistance and fire clay content

The wear resistance of the HDPE/PTFE/UHMWPE blends filled with difference concentrations of fire clay indicated by the % weight loss examination for both original and cured samples is reported in Table 6.15. Figure 6.9 is the plot of % weight loss and the fire clay contents. From the examination figures, it is seen that the % weight loss of the composite samples are clearly increased when increasing the fire clay loading for both conditioned samples. It means that lower in wear resistance of the composites are evidenced. Therefore, the materials will be easily corroded by the mechanical abrasion. The decreasing in wear resistance of the compound indicates that the adhesion between matrix and filler particles. The inferior in the wear resistance might be caused by the soft surface abrasion of the fire clay filler. The higher in the content of the softer surface filler, the lower in wear resistance, higher in % weight loss. Closer observation at the given filler loading, the fractionally increasing in the surface wear properties is noticed by the sauna treatment. It reviews that chemical inter locking via the crosslinking of polyolefin chains can withstand the filler. Therefore, the corrosion of the surface could be prevented. However, supplementation of chemical inter lock on the softer surface of the fire clay filler is not enough to increased the surface wear resistance of the obtained composite materials.

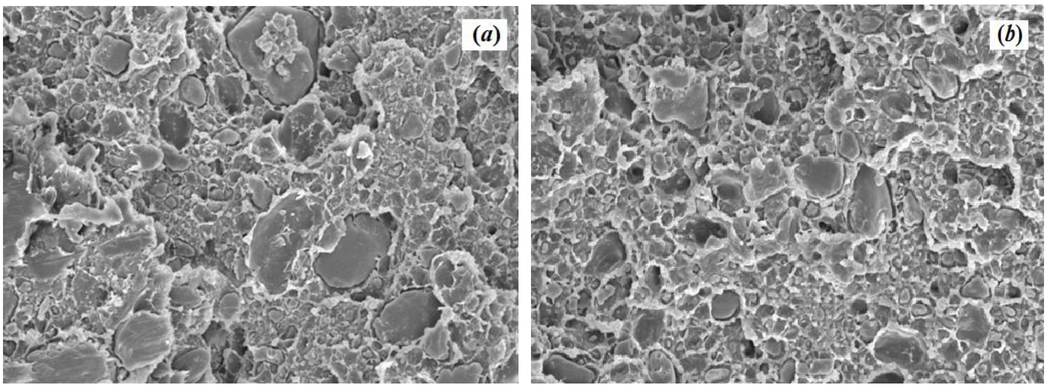
Table 6.15 Abrasive resistances of HDPE/PTFE/UHMWPE/Fire clay composites

Sample	**Weight loss (%)**	
	Original	Cured
Composite(FC# 0)	0.45±0.17	0.39±0.16
Composite(FC#10)	0.45±0.13	0.43±0.04
Composite(FC#20)	0.57±0.14	0.56±0.08
Composite(FC#30)	0.57±0.05	0.70±0.02
Composite(FC#40)	0.58±0.11	0.73±0.10
Composite(FC#50)	0.73±0.06	0.74±0.05

6.5.1.8 Morphology investigation

According to the above mechanical testing, the tensile and impact figures of the HDPE/PTFE/UHMWPE matrix filled with the fire clay particulate filler were decreased with increasing the filler loading. Flexural properties were slightly increased. The adhesion between the filler and the polymer matrix is in doubt. Therefore the SEM investigation to verify the surface adhesion in the composite is required for conclusion. The SEM photographs at X1000 of the notched impact fractured surface of the composite specimens having 0, 10, 30 and 50 phr of the filler are illustrated in Figure 6.10(***a***) to 6.10(***h***), respectively. General observation, it is obviously noticed that poor adhesion between PTFE particle and HDPE matrix is evidenced. There are large spaces between the PTFE particles for all samples. The sauna incubation slightly improves the interfacial adhesion.

Closely observation at the HDPE matrix phase, where the fire clay filler is incorporated, it is seen, especially at 10 phr of fire clay content, that the "**tougher fracture traces**" characteristic, indicated by the tailing cracking phenomena, is observed when the samples were underwent the sauna treatment. Increasing in the filler content, the "**tougher fracture traces**" become diminished. However, it is quite obvious that the interfacial adhesion between the filler and polymer matrix of the sauna cured samples is good at the fire content at 10 phr further increasing loading of the filler do inferior this adhesion. The exceed filler content would cause the inferior in the properties of the composites as observed on the above mechanical testing.



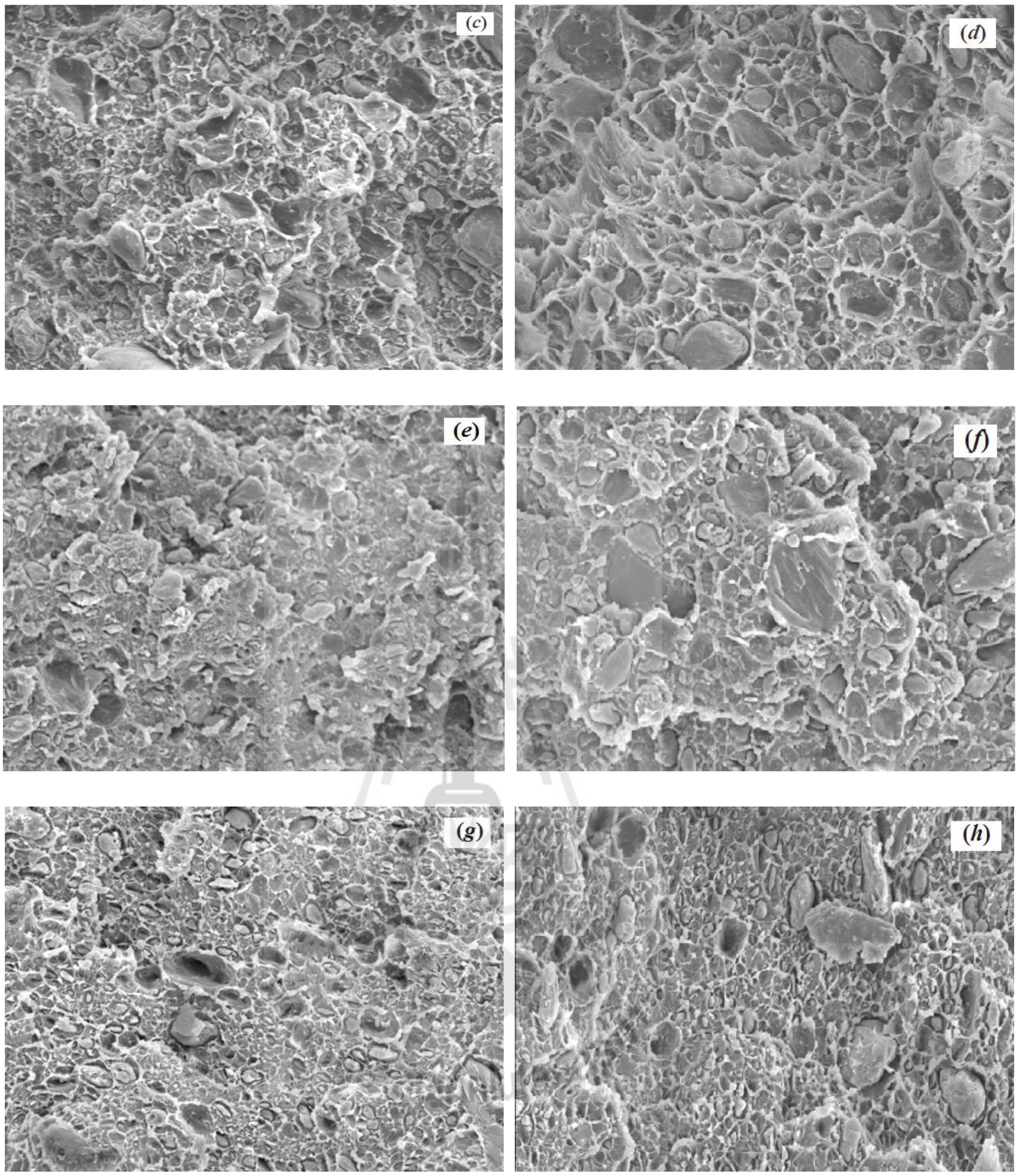


Figure 6.10 SEM micrograph of HDPE/PTFE/UHMWPE blend with different concentrations of fire clay (*a*) 0 original (*b*) 0 cured (*c*) 10.0 original (*d*) 10.0 cured (*e*) 30.0 original (*f*) 30.0 cured (*g*) 50.0 original (*h*) 50.0 cured

Within the experimental boundary and according to the test results found in this study, it could draw the statement that the MFI of the fire clay filled HDPE/PTFE/UHMWPE was increased, lower the melt viscosity, of the composite. This particulate filler could be classified as the lubricator type of filler. The mechanical and thermal properties of the composite material are slightly increased with the fire clay loading. However, the fracture toughness of the composite material was deceased with the filler addition. The adhesion between the filler and polymer matrix is taken for the explanation.

6.5.2 HDPE/PTFE/UHMWPE blend filled with binary fillers

From the previous discussion, one obvious advantage of the fire clay filler was the lubrication effect. Increasing in the fire clay content it was found that the MFI of the composite was decreased, higher in viscosity. However, the mechanical properties especially fracture toughness by mean of impact strength was slightly increased. In contrast, higher in the mineral filler in the polymer compounds would increase the melt viscosity with retaining or increasing in the mechanical and thermal properties. It would be interesting if the filler act as lubricator and also the properties enhancement. In this section, the combination between talc and fire clay filler were used as the binary filler in the ratio of 50:0, 40:10, 30:20, 20:30, 10:40 and 0:50(w/w) to be the filler in HDPE/PTFE/UHMWPE blend. The compositions of the blend compound ingredients are given in Table 6.16. DCP, silane, UHMWPE, and PTFE were retained at 1, 4.0, 5.0, and 20 phr, respectively. The HDPE/PTFE/UHMWPE blend without filler was used as reference material. The compounding procedures also the test samples preparation were achieved in the normal fashion as described in the previous segment; twin screw extruder mixer and injection molding. The effect of the hybrid filler on the properties of HDPE/PTFE/UHMWPE composite is being discussed.

Table 6.16 The blend formulation of HDPE/PTFE/UHMWPE and talc/fire clay ratios

Sample	**HDPE***(g)	**PTFE** (g) (phr)	**DCP** (g) (phr)	**Silane** (g) (phr)	**UHMWPE** (g) (phr)	**Talc** (g)	**Fire clay** (g)
Blend	400	80(20)	4(1)	16(4)	20(5)	-	-
Talc/Fire (50/0)	400	80(20)	4(1)	16(4)	20(5)	200(50)	-
Talc/Fire (40/10)	400	80(20)	4(1)	16(4)	20(5)	160(40)	40(10)
Talc/Fire (30/20)	400	80(20)	4(1)	16(4)	20(5)	120(30)	80(20)
Talc/Fire (20/30)	400	80(20)	4(1)	16(4)	20(5)	80(20)	120(30)
Talc/Fire (10/40)	400	80(20)	4(1)	16(4)	20(5)	40(10)	160(40)
Talc/Fire (0/50)	400	80(20)	4(1)	16(4)	20(5)	-	200(50)

**Total amount of HDPE including in the UHMWPE master batch*

6.5.2.1 MFI and talc/fire clay ratios

Melt flow index(MFI) of HDPE/PTFE/UHMWPE composite with the binary fillers at 230/5.0 are reported in Table 6.17 and it is also plotted and shown in Figure 6.11, respectively. From the test outcome, it is evidenced that the MFI of HDPE/PTFE/UHMWPE composite is decreased with increasing the fire clay portion or on the other word the melt viscosity is increased with decreasing the talc ratio. However, the fillers filled HDPE/PTFE/UHMWPE composite show the higher melt index value than the blend without adding the fillers. From the previous discussion, it was suggested that the fire clay filler assisted the flow ability of the blend. According to the result fond in this experimental section, combining the fire clay with talc filler it indicates that the former filler is acted as the flow retardant for the composite material. Effect of filler size could be taken into explanation. The talc used has the average particle size of 1.2 µm. Mean while the fire clay was prepared by sieving through the mesh size less than 50 µm. Normally, polymer filled with smaller filler particle would have the lower melt viscosity, higher in MFI, than filled with larger size of filler. Therefore, in this experiment higher in fire clay portion would increase the melt viscosity of the composite. However when compare with the system without filler, the fillers filled composite still has the higher flow index value than the non filled one.

Table 6.17 MFI of HDPE/PTFE/UHMWPE filled with talc/fire clay

Sample	**MFI@230/5.00**
	(g/10min)
Blend	0.071±0.041
Talc/Fire(50/0)	0.459±0.042
Talc/Fire(40/10)	0.378±0.041
Talc/Fire(30/20)	0.315±0.023
Talc/Fire(20/30)	0.233±0.032
Talc/Fire(10/40)	0.201±0.023
Talc/Fire(0/50)	0.185±0.031

6.5.2.2 HDT and talc/fire clay ratios

Service temperature of the HDPE/PTFE/UHMWPE composites measured by heat distortion temperatures at the standard load of 0.445 MPa with different ratio of talc/fire clay are reported in Table 6.18. The relationship between HDT and the fillers portion used is also graphically shown in Figure 6.11. The result reveals that the HDT of both original and cured samples are likely to be fractionally decreased with increasing the fire clay ratio. As usually found through this study, HDT of the fillers filled HDPE/PTFE/UHMWPE composites is apparently improved by the sauna incubation. Also, as commonly found for the polymeric materials, the fillers filled composite shows the superior HDT to the system without filler(s) both original and cured samples.

The slight decreasing in the HDT with increasing the fire clay proportion would be the similar phenomenon observed in the MFI test outcome. The larger particle size of fire clay, lower the specific surface area, would have the lower interfacial adhesion with the polymer matrix. Therefore, the composite material with higher fire clay portion would be more easily deformed under the thermal stress than the one having higher talc ratio. However, the degree of decreasing in the HDT, both original and cured, with the fire clay portion is very minimal. It manifests that the critical size of the fillers has no significant effect to thermal characteristic of the binary fillers filled composite.

Table 6.18 Heat deflection temperature of HDPE/PTFE/UHMWPE filled with talc/fire clay

Sample	**HDT (^{0}C)**	
	Original	Cured
Blend	60.00±1.74	67.93±0.12
Talc/Fire(50/0)	75.20±2.60	85.20±0.20
Talc/Fire(40/10)	75.80±0.40	85.20±0.20
Talc/Fire(30/20)	77.80±0.20	86.20±0.00
Talc/Fire(20/30)	76.33±0.12	85.33±0.12
Talc/Fire(10/40)	74.80±0.20	83.53±0.12
Talc/Fire(0/50)	72.93±2.12	83.13±0.23

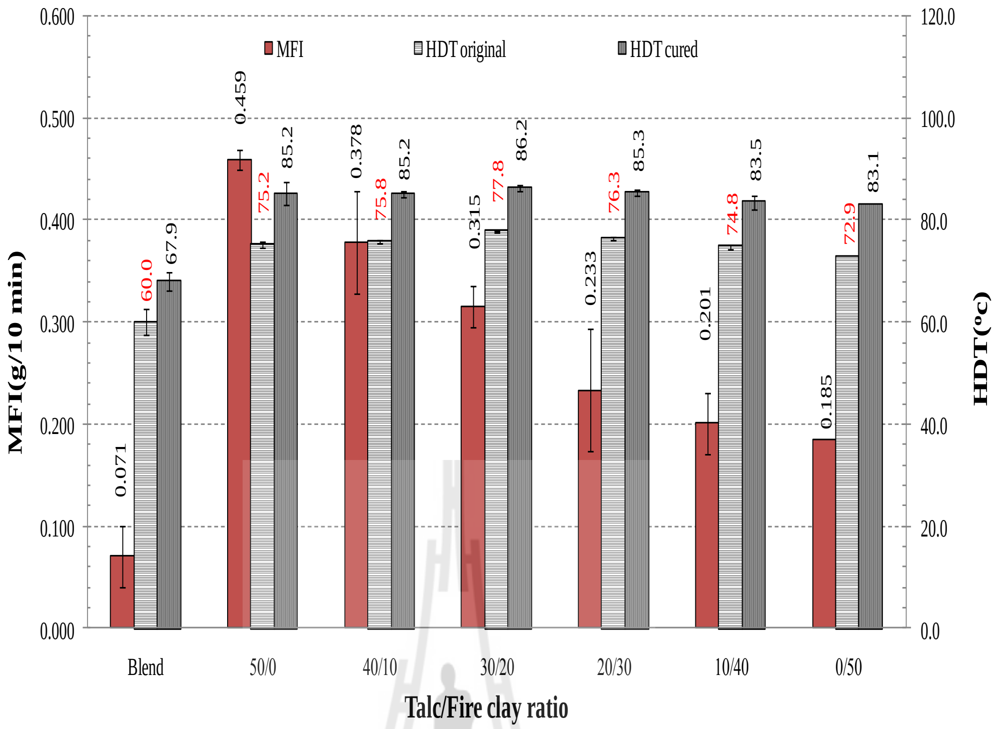


Figure 6.11 MFI and HDT of the HDPE/PTFE/UHMWPE filled with talc/fire clay

6.5.2.3 Flexural properties and talc/fire clay ratios

The flexural strength and modulus of HDPE/PTFE/UHMWPE/ composites filled with the combined fillers are summarized in Table 6.19. They are plotted with respect to the talc/fire clay ratio shown in Figure 6.12. It is observed that the flexural strength and modulus of the HDPE/PTFE/UHMWPE/fillers composite is obviously higher than the HDPE/PTFE/UHMWPE blend. Again, there is noticeable enhancement of the strength and modulus of the sample through the sauna treatment.

Within the test result of the sample using the talc/fire clay as the fillers, the bending strength of the specimen, both original and cured, is slightly increased when increasing the fire clay portion to 20 phr after that the strength is decreased with further increasing the fire clay ratio. The exact trend is found for the flexural modulus. The increasing in both flexural strength and modulus, it means that the composite with combine fillers shows the superior toughness under the bending load. The superiority in the load bending resistance of the filled polymer composite is typically enhanced by the aspect ratio of the filler. Fiber like filler with good interfacial adhesion would resolve in better flexural properties. Vice versa, rounded filler, aspect ratio close to 1.0, employed for manufacturing the polymer composite would resolve in the lower flexural characteristic than the one filled with higher aspect ratio. Regarding to the result found, it could hypothesize that the larger size of fire clay filler would have the higher in the aspect ratio. Therefore, increasing in the portion of this filler would enhance the flexural properties. However, as mention in the above section, further loading of the larger particle size, low specific area, of fire clay would cause in the interfacial incompetency. Consequently, the flexural properties would be diminished. Without the ambiguous result from this study, it could suggest that the balancing between positive effect of the filler aspect ratio and the negative influence of the interfacial adhesion must be carefully considered when two or more fillers needed in the material selection for manufacturing the polymer composite. Within this research study, the ratio between talc and fire clay binary fillers at 30/20 phr with respect to the HDPE matrix is the optimal potion for compounding the HDPE/PTFE/UHMWPE composite with good flexural properties.

Table 6.19 Flexural properties of HDPE/PTFE/UHMWPE filled with talc/fire clay

Sample	Flexural strength(MPa)		Fluxural modulus(GPa)	
	Original	Cured	Original	Cured
Blend	18.17±1.02	18.21±0.73	0.736±0.038	0.738±0.026
Talc/Fire(50/0)	29.81±0.79	30.59±1.14	1.498±0.052	1.520±0.048
Talc/Fire(40/10)	29.73±0.29	32.12±0.41	1.450±0.033	1.620±0.048
Talc/Fire(30/20)	32.69±0.42	35.38±0.59	1.632±0.027	1.812±0.053
Talc/Fire(20/30)	30.51±0.45	30.89±0.42	1.466±0.028	1.502±0.036
Talc/Fire(10/40)	28.98±0.39	30.37±0.10	1.386±0.039	1.456±0.009
Talc/Fire(0/50)	27.64±0.39	29.49±0.17	1.294±0.026	1.406±0.013

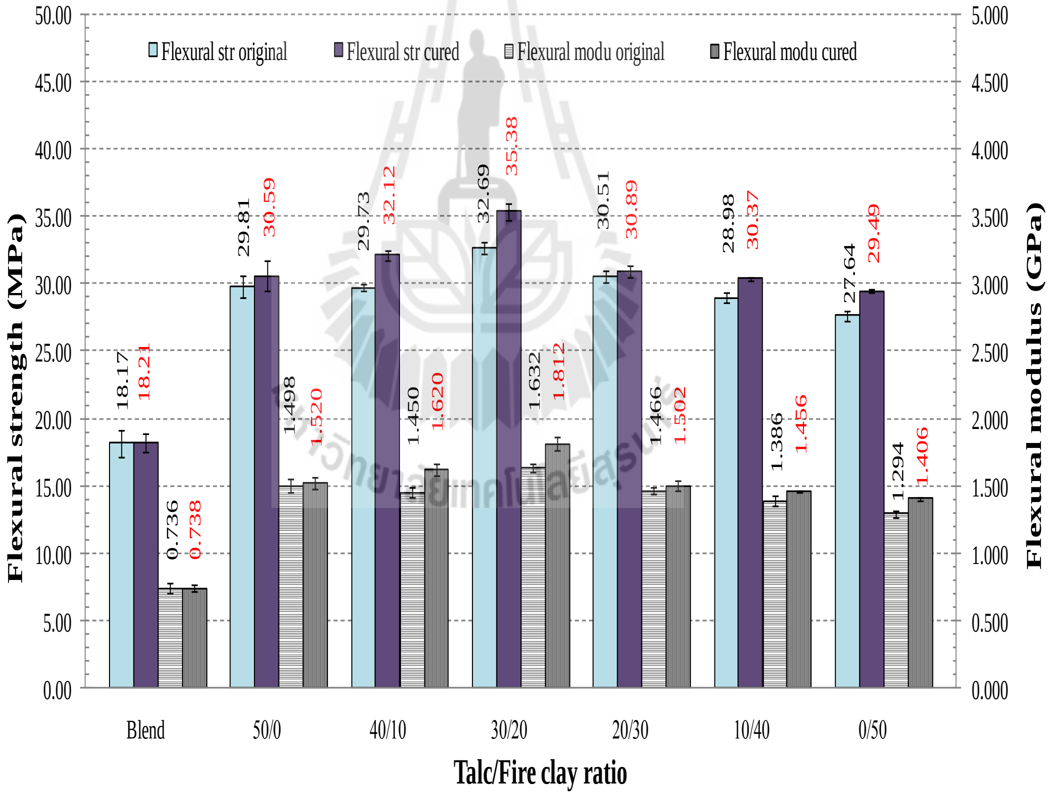


Figure 6.12 Flexural properties of HDPE/PTFE/UHMWPE filled with talc/fire clay

6.5.2.4 Tensile properties and talc/fire clay ratios

Tensile properties by mean of strength, modulus and its % elongation at break of the fillers filled HDPE/PTFE/UHMWPE at strain rate of 50 mm/min are given in Table 6.20. Mean while, Figure 6.13 is the plot between the strength and modulus and the ratio of talc/fire clay filler. From the test values obtained, it is seen that the strength and modulus of both original and cured samples are improved by adding the filler(s) regarding to the unfilled sample. It is quite typical for the polymeric material where the mechanical properties are superior by adding the mineral filler(s).

Considering the relationship between the strength and modulus of the composite material with the talc/fire clay ratio, it is seen that both the tensile properties, strength and modulus, are obviously decreased with increasing the fire clay fraction or, in the other word, they are increased with increasing the talc ratio. The decreasing in these properties with increasing fire clay loading could be one of the facts that, earlier mentioned, the bigger in the average size of the fire clay than the talc. The larger of the particle size the smaller in the specific area. Then, the inferior in the interfacial surface adhesion would be experienced. The tension properties would be diminished.

Performing the sauna treatment of the samples, at the given talc/fire clay ratio, the results manifest that the tensile strength and modulus are better than the system without the treatment. Not only the enhancement in the material crystallinity but also the outcome of silane/moisture condensation reaction; chain crosslink and interfacial adhesion, have the positive effect on the tensile characteristics.

Figure 6.14 shows the relationship between % elongations at break and talc/fire clay ratio contained in HDPE/PTFE/UHMWPE blends. It is seen, both original and cured samples, that the % elongation of the filler filled blends is dramatically decreased when filler and the combined fillers were added. Typically, mineral filler addition has a negative effect to the flexibility or ductility of the polymeric material. The more of filler added the lesser in the % elongation. Closer investigation between the fillers ratio and the % elongation at break, it is noticed that the break point of the sample is fractionally increased when increasing the fire clay. The obvious increasing in the yield point is observed from the composite sample derived from 50 phr of only fire clay filler. It is indicated that higher in the aspect ratio of fire clay filler than talc would be lined in parallel with the flow direction. Then, with decent adhesion, increasing in the deformation would be obtained by applying the tension loading in the longitudinal direction with the filler alignment. The % elongation at break also reveals that the number is lower on the sauna cured specimen than the original one. Again, increasing in the crystallinity while prolong annealing and crosslinked chain through the silane/moisture induce crosslink condensation reaction are responsible for the less deformation of the sample.

From the tensile properties of the HDPE/PTFE/UHMWPE filled with talc, fire clay and combination of talc/fire clay fillers obtained, it was found that the tension properties of the composite material was superior when adding the filler(s). However, the mechanical properties of the composite filled with combined fillers were inferior when increasing the fire clay fraction. The main drawback of the fire clay filler is the larger in the particle size.

Table 6.20 Tensile properties of HDPE/PTFE/UHMWPE filled with talc/fire clay

Sample	**Tensile strength(MPa)**		**Tensile modulus (GPa)**		**Elongation at break (%)**	
	Original	Cured	Original	Cured	Original	Cured
Blend	15.60±0.29	16.28±0.17	0.582±0.049	0.580±0.038	67.30±11.09	67.17±7.10
Talc/Fire(50/0)	20.22±0.62	21.51±0.34	1.436±0.059	2.018±0.059	4.49±0.33	3.23±0.13
Talc/Fire(40/10)	17.42±0.15	19.77±0.62	1.394±0.040	2.176±0.093	3.67±0.36	2.43±0.10
Talc/Fire(30/20)	18.01±0.47	18.46±0.18	1.338±0.029	1.718±0.023	3.90±0.25	2.71±0.18
Talc/Fire(20/30)	17.92±0.51	19.17±0.9	1.230±0.034	1.648±0.077	4.59±0.35	3.35±0.15
Talc/Fire(10/40)	17.28±0.15	18.14±0.23	1.062±0.061	1.444±0.060	5.98±0.37	4.48±0.17
Talc/Fire(0/50)	17.10±0.19	17.86±0.23	1.016±0.044	1.044±0.037	8.12±1.04	8.20±0.24

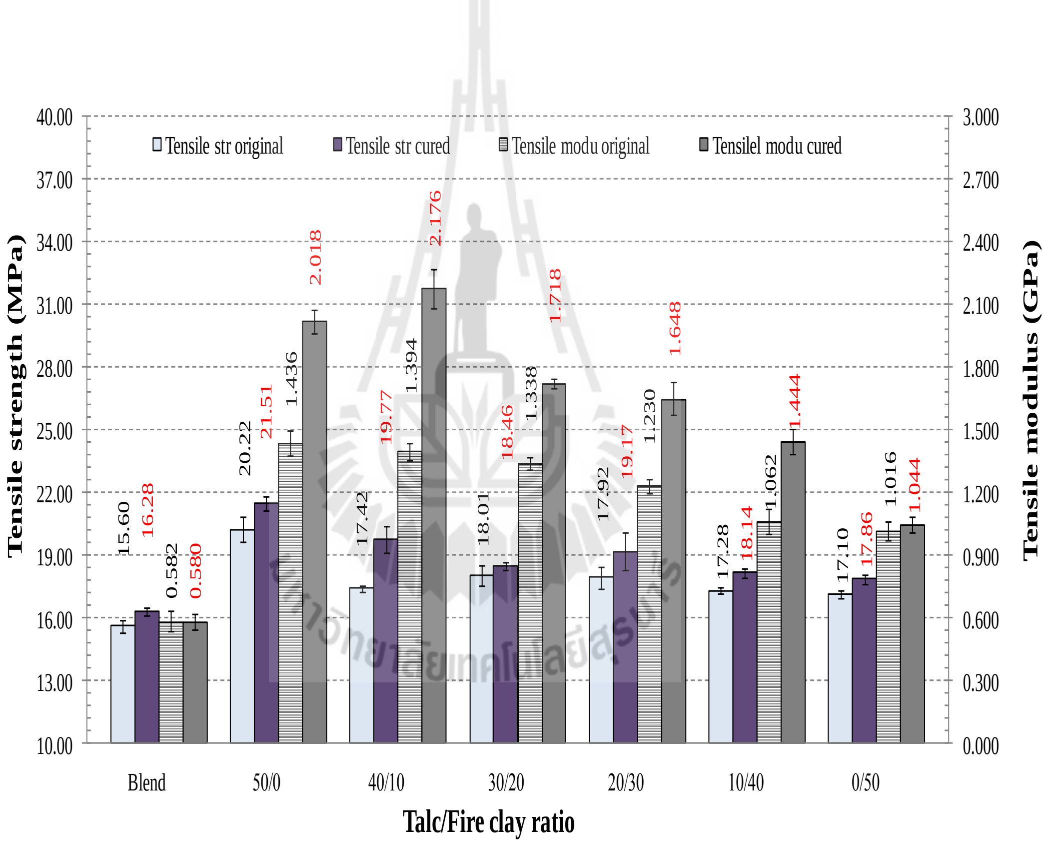


Figure 6.13 Tensile strength and modulus of HDPE/PTFE/UHMWPE filled with talc/fire clay

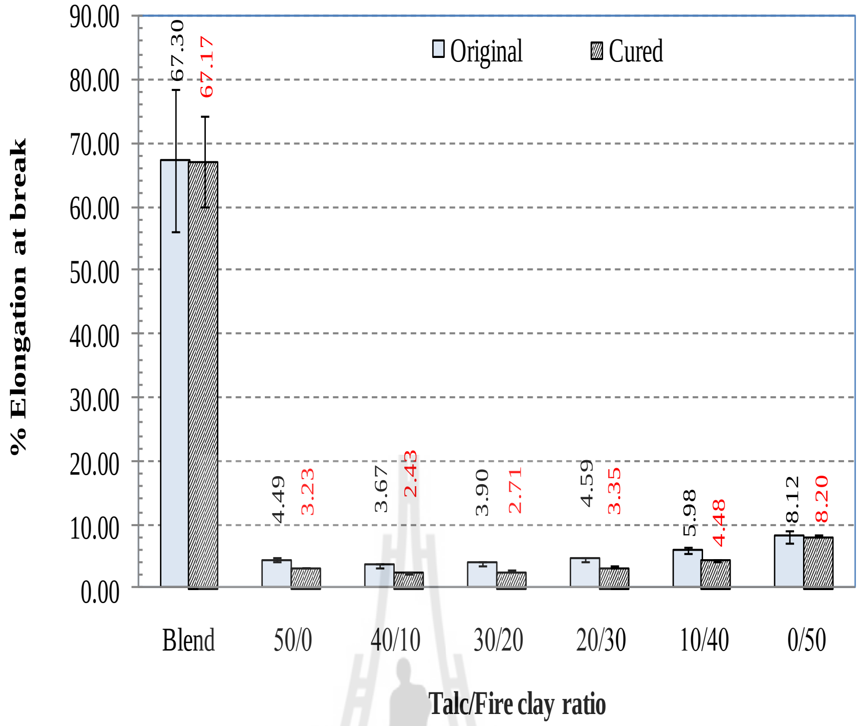


Figure 6.14 Elongation at break of HDPE/PTFE/UHMWPE filled with talc/fire clay

6.5.2.5 Impact strength and talc/fire clay ratios

From the above investigation found that bending toughness under flexural strain and the toughness under the tension loading of the HDPE/PTFE/UHMWPE composite material at 50 phr of the filler loading were tendency to be decreased with increasing the fire clay fraction. Again, the fracture toughness of the composite by mean of the impact strengths for both original and cured samples were conducted. The notched impact strength of the samples is reported in Table 6.21, and they are used to plot against the talc/fire clay ratio shown in Figure 6.15. For the unnotched strength, it was found that the specimen was not broken at the given pendulum load at 5.4 J. Therefore, the impact strength number cannot be calculated.

For the notched impact strength outcome, it is observed that the notched impact strength of the blend without filler(s) is much higher than the blend with adding filler(s). This is quite common observation where the impact toughness of the polymeric material is inferior by adding the particulate filler. However, at the filler(s) content at 50 phr, it is obviously seen that the impact strength is increased with higher the fire clay portion. There are two hypothesizes to explain this superiority. The high aspect ratio of the fire clay as discussed earlier. Moreover, the possibility that fracture interfacial adhesion between the polymer matrix and fire clay is higher than that of between polymer/talc. Therefore, the toughness of the fire clay composite is superior than the talc one. With these two characteristics without scarifying the interfacial adhesion, adding the fire clay into the HDPE/PTFE/UHMWPE blend would enhance the impact strength. Comparing the composite samples with and without sauna treatment, the impact result reveals that the strength is lowered after undergoing the treatment. The examination figures tell that the impact toughness is scarified by the higher in the crystallinity and also the crosslink density via the silane/moisture condensation.

According to the impact investigation in this study, the results indicate that the filler(s) loading at 50 phr was decreased the impact toughness of HDPE/PTFE/UHMWPE blend. On the other hand, increasing the ratio of fire clay in the combined talc/fire clay fillers found that the impact strength of the fillers filled composite was improved. The higher in filler aspect ratio and better toughness of fire clay than the talc was taken into consideration.

Table 6.21 Impact strengths of HDPE/PTFE/UHMWPE filled with talc/fire clay

Sample	**Notched (kJ/m^2)**	
	Original	Cured
Blend	5.31±0.47	5.81±0.14
Talc/Fire(50/0)	2.97±0.05	2.59±0.13
Talc/Fire(40/10)	3.36±0.08	2.73±0.10
Talc/Fire(30/20)	3.53±0.07	2.79±0.12
Talc/Fire(20/30)	3.55±0.10	2.94±0.20
Talc/Fire(10/40)	3.57±0.04	3.17±0.04
Talc/Fire(0/50)	5.24±0.12	4.31±0.06

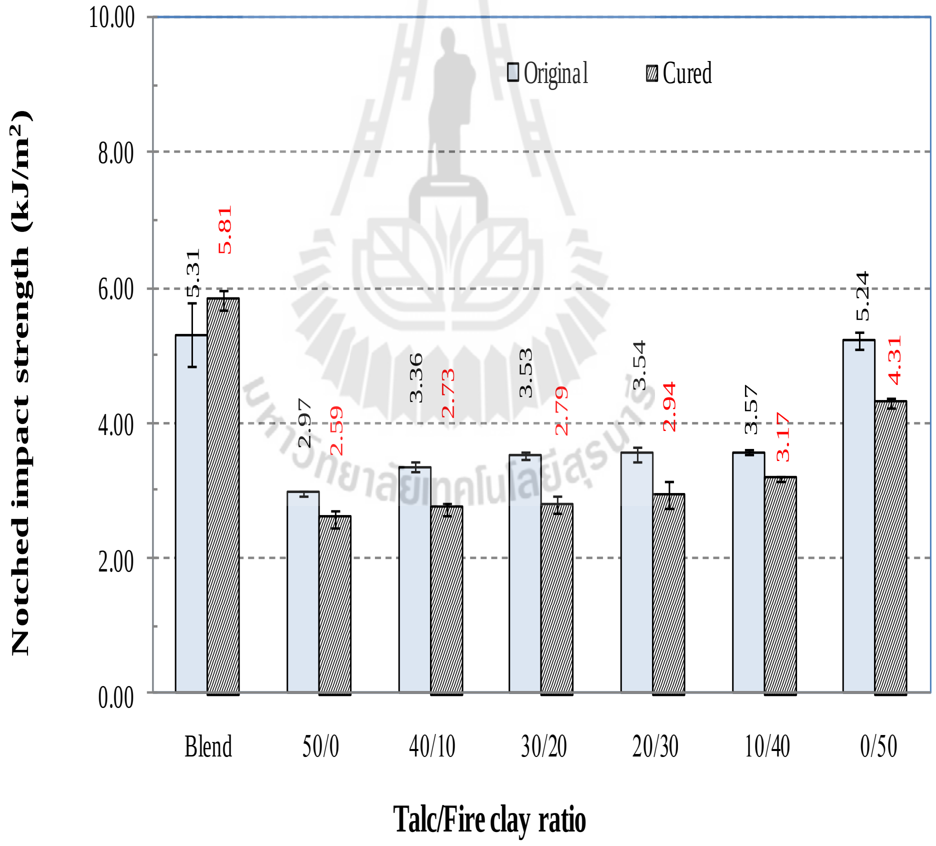


Figure 6.15 Notched impact strength of HDPE/PTFE/UHMWPE filled with talc/fire clay

6.5.2.6 Water drop diameter and talc/fire clay ratio

Surface tension of HDPE/PTFE/UHMWPE and filler(s) composite by means of measuring the ratio of water drop diameter on the sample (D_{sample}) and on the PTFE reference (D_{PTFE}) for the original and cured composites are summarized in Table 6.22 and they are also plotted with respect to the talc/fire clay portion in Figure 6.16. General observation and also taken the standard deviation into account, the result indicates that there is no significantly change in the D_{sample}/D_{PTFE} ratio. The measure ratios are more than 1.00. It reveals that the diameter of water on the sample is bigger than on the PTFE reference. It means that the HDPE/PTFE/UHMWPE composite has high surface tension to water than on the Teflon sheet. Comparison between original and cure samples at the given filler(s), it seen that the values obtained from cured sample are marginally lower than the original ones. It manifests that the surface tension of the composite is fractionally lower when the sample were undergone sauna treatment. Again, it would be ambiguous to state that crosslinking and crystallinity are responsible for the minor improvement because the degree in superiority is marginally.

Typically, the hydrophillicity of talc is lower than fire clay. Then, the surface tension of water on talc must be higher than on the fire clay. Therefore, adding talc into polymer matrix would higher the surface tension of the material if the filler is homogenously mixed and dispersed on the surface of the test specimen. No significantly change in the surface tension of the talc/fire clay filled HDPE/PTFE/UHMWPE composite could be due to the fact that the filler(s) is homogenously mixed with the polymer matrix and the most of filler(s) particle is throughoutly covered with polymeric film. Consequently, the surface tension characteristic of filler is inhibited and only the characteristic of the polymeric is dominated.

Table 6.22 Water drop diameter of HDPE/PTFE/UHMWPE filled with talc/fire clay

Sample	**D_{sample} /D_{PTFE}**	
	Original	Cured
Blend	1.13±0.03	1.12±0.01
Talc/Fire(50/0)	1.10±0.03	1.06±0.02
Talc/Fire(40/10)	1.08±0.03	1.05±0.02
Talc/Fire(30/20)	1.09±0.02	1.05±0.04
Talc/Fire(20/30)	1.09±0.02	1.05±0.03
Talc/Fire(10/40)	1.09±0.02	1.06±0.03
Talc/Fire(0/50)	1.12±0.03	1.08±0.02

6.5.2.7 Abrasive resistance and talc/fire clay ratio

The wear resistance of HDPE/PTFE/UHMWPE composite filled with combined fillers by means of % weight loss for both original and cured samples are summarized in Table 6.23 and graphically presented in Figure 6.16. From the test result, it is undoubtedly seen that, the % weight loss of the filler(s) filled HDPE/PTFE/UHMWPE composite are higher than the blend, without filler. With respect to the effect of fire clay fraction for the composite samples, it indicates that the % weight loss is trendily increased with increasing the fire clay portion. The highest %, 0.87, is found when only 50 phr of fire clay is used. The larger particle size of fire clay than the talc and also the lower in the interfacial adhesion would be taken into explanation. Composite made from the large particle size filler in which the polymer/filler interfacial adhesion would be inferior and hence lower in the wear resistance.

At the given filler and combined fillers, the examination outcome also shows that the % loss of sauna cured sample is higher than the original one. The result is contradicted with the HDPE/PTFE/UHMWPE blend where the sauna incubation is superior the wear resistance of the material. Adding filler(s) into the silane/moisture induced polymer matrix would retard the chain crosslink during the incubation process. Because of the filler particle would act as the physical barrier between the initiated chains. As the result lower crosslink density is obtained. Consequently, the lower in the physical interlock on filler particle is diminished. The filler would be easily abraded during the wear process.

Table 6.23 Abrasive resistances of HDPE/PTFE/UHMWPE filled with talc/fire clay

Sample	**Weight loss (%)**	
	Original	Cured
Blend	0.43±0.03	0.27±0.02
Talc/Fire(50/0)	0.60±0.02	0.76±0.02
Talc/Fire(40/10)	0.61±0.04	0.78±0.03
Talc/Fire(30/20)	0.70±0.01	0.81±0.02
Talc/Fire(20/30)	0.71±0.04	0.83±0.03
Talc/Fire(10/40)	0.84±0.01	0.85±0.04
Talc/Fire(0/50)	0.87±0.03	0.92±0.01

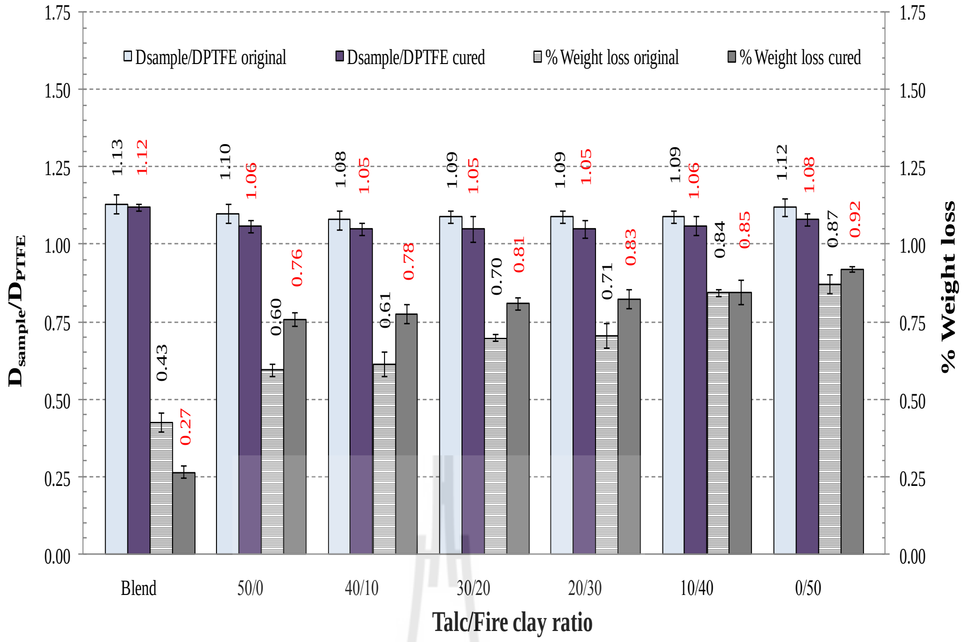


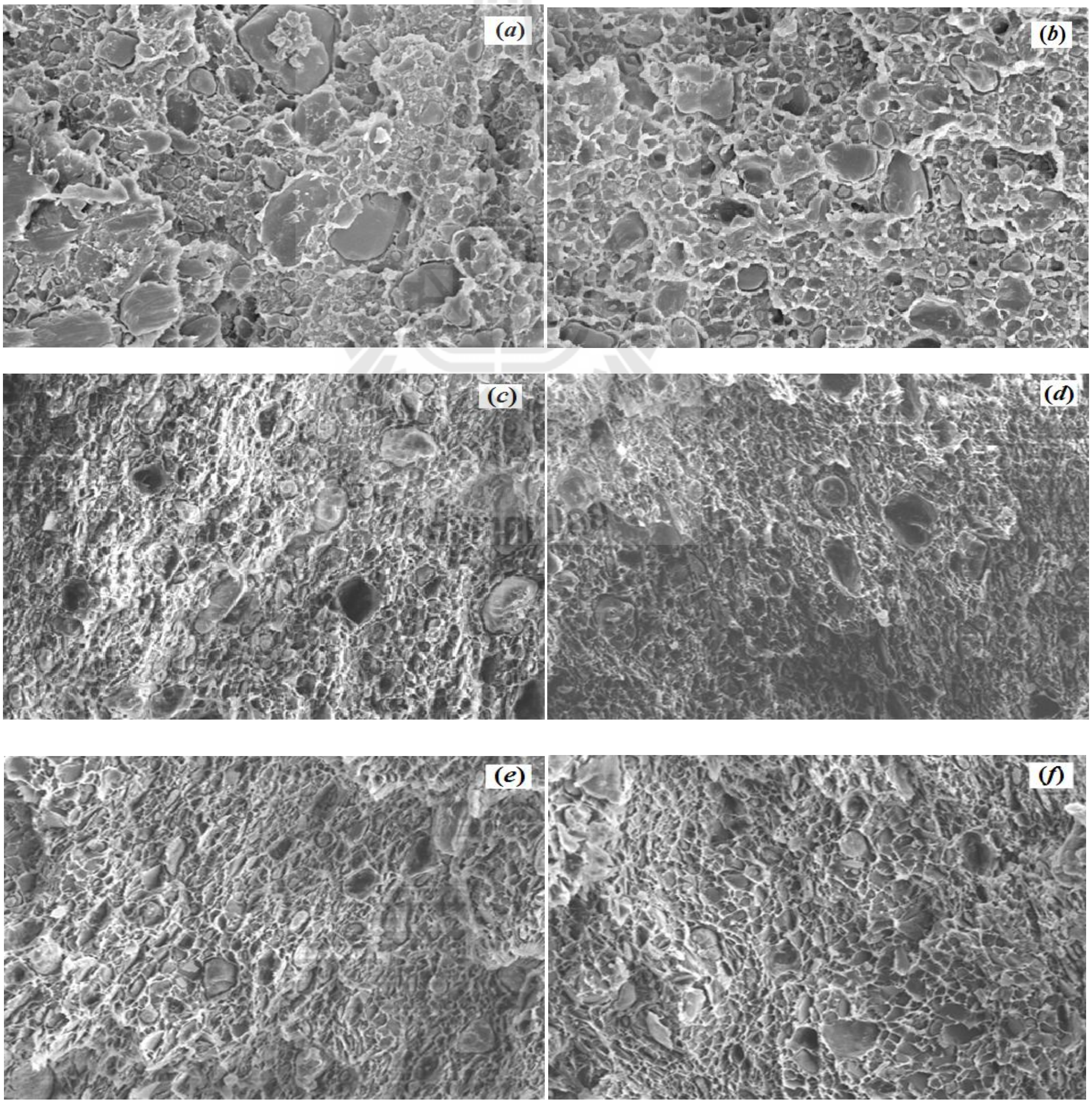
Figure 6.16 Surface tension and abrasive resistance of HDPE/PTFE/ UHMWPE filled with talc/fire clay

6.5.2.8 Morphology investigation

From the above discussion, the term interfacial adhesion between the HDPE/PTFE/UHMWPE matrix and filler(s) were occasionally taken into hypothesized. Visual observation on the interfacial adhesion between those two materials is necessary. So, the SEM photographs of the fractured surface obtained from notched impact specimen of the selected samples, both original and cured, are summarized in Figure 6.17(***a***) to 6.17(***f***), respectively. At the magnificent of X1,000, only the interfacial between larger particle of PTFE and HDPE/UHMWPE is clearly observed. The added filler(s) seem to be finely dispersed into the HDPE/UHMWPE phase. Taken the filler or fiber pull out phenomenon into consideration, from the SEM images, it is seen that there is hardly seen the evidence of the filler pull out on the fractured surface of the HDPE/PTFE/UHMWPE blend. Vice versa, there are some pull out traces on the surface of the filler(s) filled composites. It is indicated that worst surface adhesion of PTFE/HDPE matrix when adding filler(s). The observation is in agreement with the impact strength of the samples where the blend showed the higher strength than the composite. At this stage, the primary conclusion would be written that the properties of the filler(s) filled HDPE/PTFE/UHMWPE composite are dominated by the adhesion between PTFE and the matrix. Therefore, added ingredient onto the HDPE mixture matrix that effect on the adhesion between PTFE particle and the homogenous phase would have the significant influence on the overall properties of the composite material.

Then, by closer investigation on the effect of filler(s) in the continuous HDPE filled phase, Figure 6.17(***c***) to 6.17(***j***) are the filler filled composites obtained by decreasing the talc ratio from 50/0, 30/20, 10/40 and 0/50, respectively. According to the impact testing result, the impact strength was increased with decreasing the talc portion, or on the other word, it is increased with increasing the fire clay fraction. By looking at the fracture traces on the HDPE matrix phase in which the filler(s) were incorporated, it is seen that the fibril formation, or “trailing cracking phenomena” are more obvious when the fire clay portion is increased. This phenomenon is normally a sign of toughening enhancement as described in the previous discussion. The trailing observation is more dominantly seen when the samples were undergone sauna treatment. According the SEM observation, one of hypothesizes could be stated that the loosely chain network is probably and easily formed when the fire clay portion is increased. Because of fire clay has larger particle than the talc filler. Therefore, more flexible, high impact toughness, in the loose fire clay filled crosslink than the tight talc filled crosslink HDPE/UHMWPE blend matrix.

Taken PTFE/matrix interfacial adhesion and toughening of the filler(s) filled matrix into accountability, it could say that the matrix toughening effect is more dominate than the negative interfacial adhesion. The improvement in the fracture toughness by the flexibility of the loose crosslink is final verdict for the fire clay/talc filled HDPE/PTFE/UHMWPE composite.



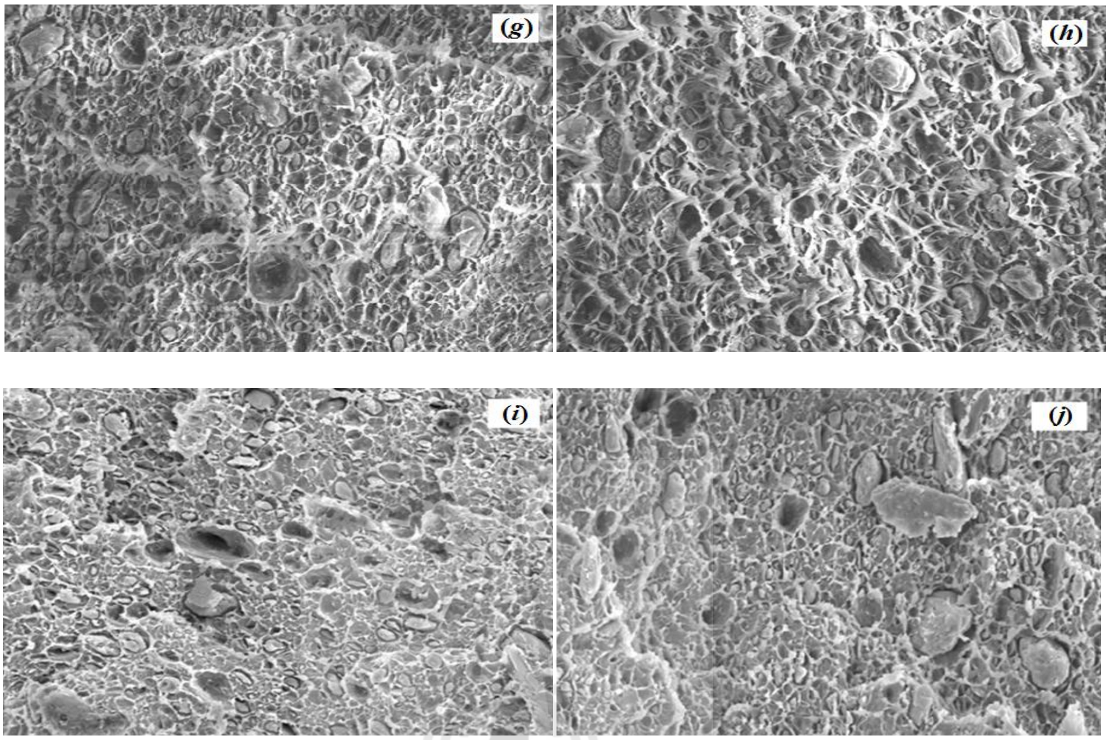


Figure 6.17 SEM micrograph of HDPE/PTFE/UHMWPE blend filled with different ratios of talc/fire clay (*a*) blend (original), (*b*) blend (cured), (*c*) Talc/Fire(50/0) (original), (*d*) Talc/Fire(50/0) (cured) (*e*) Talc/Fire(30/20) (original), (*f*) Talc/Fire(30/20) (cured), (*g*) Talc/Fire(10/40) (original), (*h*) Talc/Fire(10/40) (cured), (*i*) Talc/Fire(0/50) (original), (*j*) Talc/Fire(0/50) (cured)

For future improvement of the flow ability of the talc filled HDPE/PTFE/UHMWPE composite by adding the in house fire clay filler, it was found that the flow index of the composite did not increased, lower in viscosity, by increasing the fire clay fraction. It was also found that the fire clay filler did not have the significant effect on the HDT of the composite. Moreover, the mechanical properties by mean of tensile and flexural were also slightly inferior when high portion of fire clay was used. The impact toughness was slightly increased with increasing the fire clay ratio. The surface properties both wear and tension were not obviously affected by the fire clay filler. The larger particle size of the fire clay than talc is taken into explanation.

6.5.3 Peeling investigation

One of the main applicable goals for this research work is the innovating material having low surface tension to the polar liquid. Therefore, the material can be applied to vast variety of application. One of the intentionally application is non stick plastic cup for harvesting the natural rubber latex to reduce the stick on rubber lump. Hence, high yield harvesting and minimal cleaning time would be benefit for the rubber agricultures. To verify the advantage of the inspired material, the peel test must be examined. The required force for peeling the "**adherent**" and the HDPE/PTFE/UHMWPE substrate samples were measured to evaluate the peeling strength. The testing is adopted in accordance with the ASTM D903. Two types of adherent were performed in this study, the commercial single side sticky tape and actual rubber crepe. The tape film and dried rubber were coated on the surface of the injected bar polymer samples as shown in Table 6.42. They are including; neat HDPE, silane/DCP induced crosslinked HDPE (xHDPE), HDPE/PTFE blend (Blend (Sil4.0)), HDPE/PTFE/UHMWPE blend (Blend UH 5.0), talc filled HDPE/PTFE/UHMWPE (Talc/Fire (0/50)), fire clay filled HDPE/PTFE/UHMWPE (Talc/Fire (50/0)) and talc/fire clay filled HDPE/PTFE/UHMWPE (Talc/Fire (30/20)), respectively. The HDPE composite filled with 30/20 talc and fire clay was selected for the test because its properties; both mechanical and surface, were relatively decent. If the commercial trial is required, this HDPE composite formula would be chosen for the pilot scale application. Again, PTFE/fiber glass sheet is used as the referee. The detail for test samples preparation and the method for performing the test were described in the experimental section, 6.4.3.3.

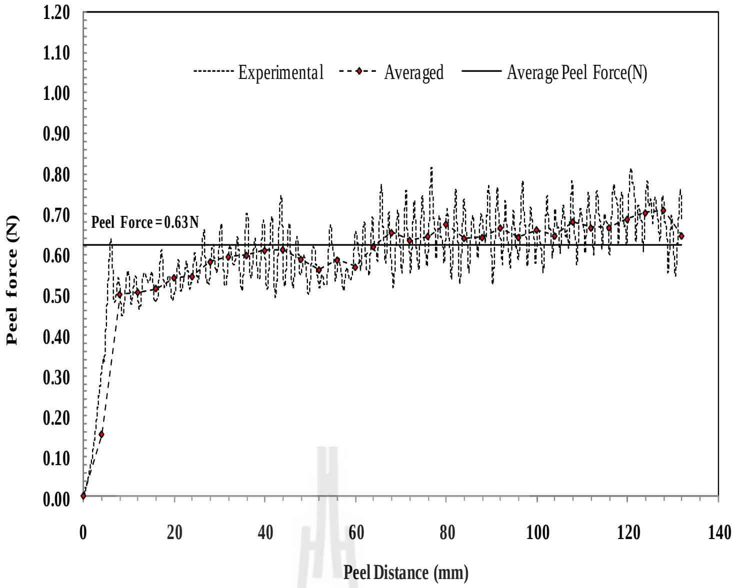
Table 6.24 The compositions of each compound ingredients

Samples	**HDPE**(g)	**DCP** (g) (phr)	**Silane** (g) (phr)	**PTFE** (g) (phr)	**UHMWPE** (g) (phr)	**Fire clay** (g) (phr)	**Talc** (g) (phr)
PTFE sheet	-	-	-	-	-	-	-
HDPE	400	-	-	-	-	-	-
xHDPE	400	4(1)	16(4)	-	-	-	-
Blend(Sil 4.0)	400	4(1)	16(4)	80(20)	-	-	-
Blend(UH 5.0)	367	4(1)	16(4)	80(20)	20(5)	-	-
Talc/Fire (0/50)	367	4(1)	16(4)	80(20)	20(5)	(50)(200)	-
Talc/Fire (50/0)	367	4(1)	16(4)	80(20)	20(5)	-	(50)(200)
Talc/Fire (30/20)	367	4(1)	16(4)	80(20)	20(5)	(20)(80)	(30)(120)

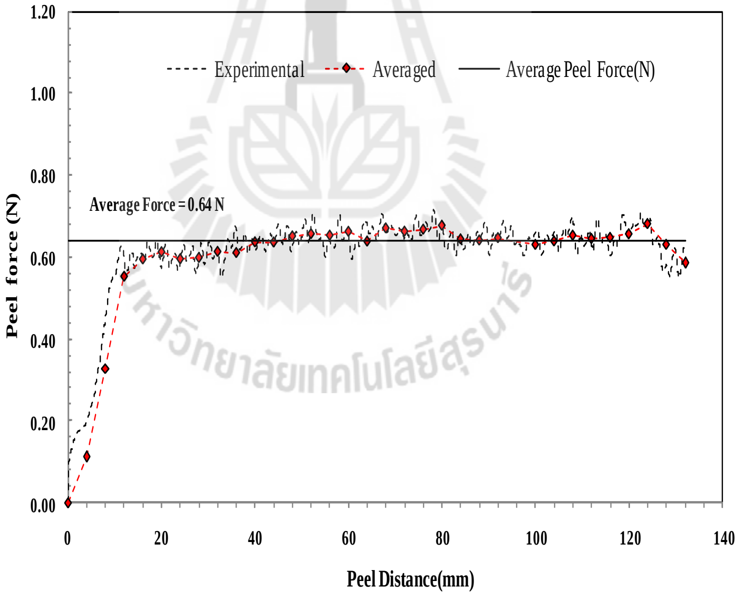
The peel force or stripping strength for the assigned samples was conducted. Figure 6.18 and 6.19 are the selected graphically demonstrate of the peeling test result using the commercial adhesive tape and actual dried rubber crepe, respectively. The adhesive would represent the higher polarity adherent than the natural rubber crepe. Commonly, the tape is easily to adhere in vast variety of surfaces ranging from oily surface to paper carton. Approximately 4 mm peeling distance were manually averaged and re-plotted. Finally, the approximate maximum peeling force was taken as peeling force(N) at the given adherent. The rest of the samples were conducted in the exact manner. Table 6.25 summarizes the peel forces using adhesive tape and rubber crepe as adherents on the polymer samples. They are also graphically shown in Figure 6.20.

From the peel forces obtained both on the commercial adhesive tape and the dries rubber crepe, it is generally indicated that the peeling force obtained using adhesive tape is much higher than from the dried rubber crepe. It is also notice that the force does not depend on the sample conditioning. Test figures obtained from the original specimen are close to the numbers derived after the sauna treatment for both adherents. Going back to the selected peeling test graphs, it was also observed that the peel forces over the adhesive tape were tidier than the ones performed on the real dried rubber. This was because transforming the latex into dried crepe was time consuming, more than a week. During the drying process, the protein rotted and fermentation was taken place. They would have the significant effect to the surface adhesion between the rubber and the polymer samples. Consequently, the resulted peel forces were uneven comparing with the adhesive tape. However, in generally, it is clearly seen that the lowest peel force is found when the commercial PTFE sheet was used as the substrate for both adherents; approximately 0.63±0.07 N on the adhesive and 0.13±0.03 N on the rubber, respectively.

For the examination performed on the adhesive tape, the results show that the peeling force is increased from virgin HDPE to silane/DCP induced crosslinked HDPE (xHDPE). Further increasing in the peeling resistance when the silane content was increased to 4.0 phr, Blend (Sil 4.0), and 5.0 phr of UHMWPE, Blend (UH 5.0), was added. For the talc and fire clay filled HDPE/PTFE/UHMWPE composites, it is noticed that the peeling forces are close to the HDPE. Especially when 30 part of talc mixed with 20 part of fire clay was used as the combined filler. The peeling force is gone down to 0.68±0.02 N for the original composite. According the outcome found, it could suggest that adding crosslink agent, especially silane, would enhance the surface polarity. Consequently, the interfacial adhesion between polymer substrates and the assigned adherent would be promoted. Vice versa, adding the lower polarity filler(s) into the blends would retard the surface adhesion. Taken this research study into consideration, the added filler(s) not only reduce the surface polarity but also enhance the surface smoothness of the samples. It was observed that, without filler(s) addition, the surface of the highly crystalline polymers blend were rough because the large volume shrinkage due to the transition from the molten amorphous to highly crystalline solid via the cooling stage. This uneven surface would generate the mechanical interlock between substrate and adherent. Therefore, higher peeling force, than the smoother surface, would be experienced.

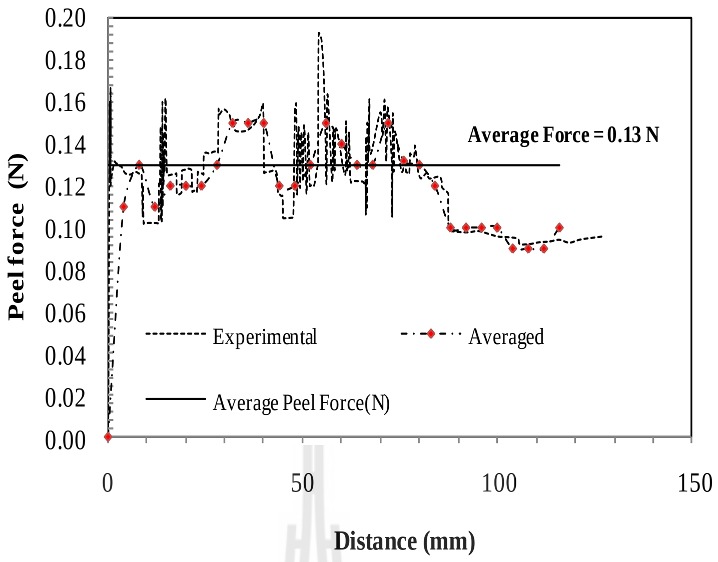


(a)

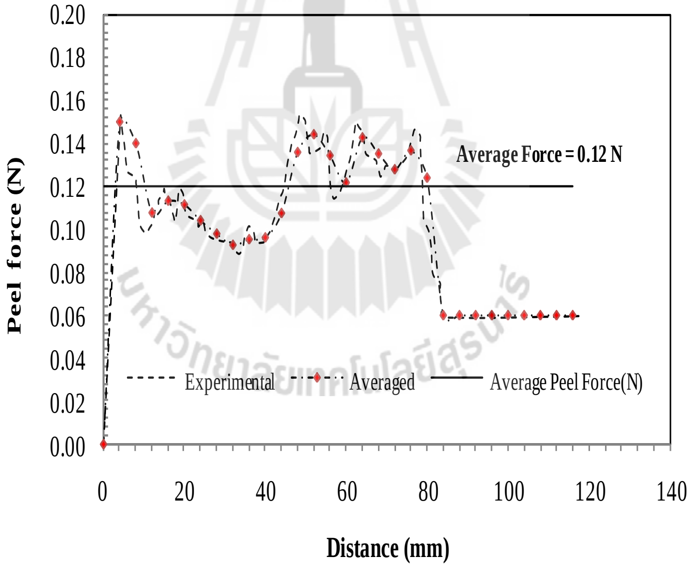


(b)

Figure 6.18 Peeling forces and distance of the adhesive tape on; (*a*) PTFE sheet, (*b*) HDPE/PTFE/UHMWPE filled with 30:20 talc/fire clay(cured)



(a)



(b)

Figure 6.19 Peeling forces and distance of dried natural rubber crepe on; (*a*) PTFE sheet, (*b*) HDPE/PTFE/UHMWPE filled with (30:20) talc/fire clay(cured)

Table 6.25 Summary of the peel forces

Sample	**Peel Force**(N) **on Adhesive Tape**		**Peel Force**(N) **on Rubber Crepe**	
	Original	Cured	Original	Cured
PTFE sheet	0.63±0.07	na	0.13±0.03	na
HDPE	0.66±0.03	na	0.17±0.03	na
xHDPE	0.72±0.03	0.68±0.03	0.19±0.04	0.19±0.03
Blend(Sil 4.0)	0.76±0.02	0.75±0.02	0.19±0.02	0.18±0.03
Blend(UH 5.0)	0.77±0.03	0.69±0.01	0.18±0.04	0.15±0.01
Talc/Fire (0/50)	0.69±0.01	0.64±0.01	0.14±0.01	0.12±0.01
Talc/Fire (50/0)	0.69±0.02	0.65±0.02	0.15±0.02	0.13±0.02
Talc/Fire (30/20)	0.68±0.02	0.64±0.02	0.14±0.02	0.12±0.07

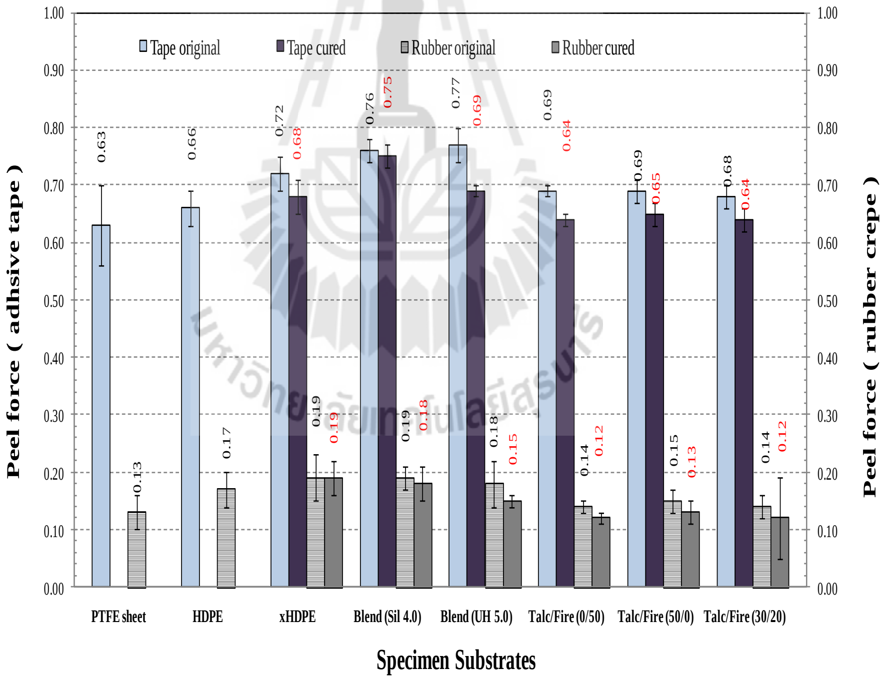


Figure 6.20 Peeling forces and distance of adhesive Tape and natural rubber crepe on the test specimens

In the case of real application testing, the dried rubber was coated on the test samples including HDPE, xHDPE, HDPE/PTFE/UHMWPE filled with talc/fire clay specimen and PTFE referee, respectively. The actual relationship between the peeling force and distance on the PTFE and 30/20 talc/fire clay filled HDPE/PTFE/UHMWPE are demonstrated in Figure 6.19 and the averaged peel forced were calculated. The rest of the samples were performed in the exact manner. Table 6.25 and in Figure 6.20 are the summarization of the calculated peeling force obtained from the test specimens. Again, when compare the figures with the adhesive tape, it was clearly seen that the peeling force for the dried rubber crepe is much lower than the adhesive tape for the given sample. As mention earlier, both poor quality of the crepe formed and also lower polarity of the dried rubber than the tape would be taken into explanation.

Considering from the test outcome for the original samples, the lowest peeling force, 0.13±0.03 N, is obtained from the PTFE referee. It is also noticed that the peeling force is gradually decreased from HDPE to 30/20 talc/fire clay filled composite. On the sauna cured substrates, the similar trend is also evidenced. The lowest peeling force at 0.12±0.07 N is obtained when 30/20 talc/fire clay filler were added into the crosslinked HDPE/PTFE/UHMWPE composite. The previous explanation written for adhesive tape would be adopted for manifesting the peeling result derived using the rubber crepe as adherent.

According to the applicable research investigation, peel test, it could suggest that the lower peeling resistance was obtained while adding low polarity fillers onto the crosslinked HDPE/PTFE/UHMWPE. The easiness for removing the rubber crepe from the surface was equated to the low surface tension of PTFE. The smoothness surface due to the lower molding shrinkage and low polarity of the fillers were taken into explanation.

6.6 Conclusion

The talc and fire clay powder were employed as the fillers to investigate their influence on the flow ability, mechanical and also surface properties of the HDPE compound. By using only fire clay as filler, it was fond that the MFI of the fire clay filled HDPE/PTFE/UHMWPE composite was increased, lower in the melt viscosity of the composite. Fire clay filler acted as the lubricator type of filler. The mechanical and thermal properties of the composite material were slightly increased with increasing the fire clay loading. However, the fracture toughness of the composite material was deceased. The adhesion between the filler and polymer matrix was taken for the explanation.

Future investigation by using combined fillers between the in-house fire clay and talc fillers in the HDPE/PTFE/UHMWPE composite, it was found that the melt flow index of the composite did not increased by increasing the fire clay fraction. It was also found that the fire clay filler did not have the significant effect on the HDT of the composite. Moreover, the mechanical properties by mean of tensile and flexural were also slightly inferior when high portion of fire clay was added. The impact toughness was slightly increased with increasing the fire clay ratio. The surface properties both wear and tension were not obviously affected by the fire clay filler. The larger particle size of the fire clay than the talc was taken into explanation.

For the peeling force investigation on the surface of the blends, it was evidenced that the lower peeling force was obtained while adding low polarity fillers, 30/20 talc and fire clay, onto the crosslinked HDPE/PTFE/UHMWPE. The easiness for removing the rubber crepe from the surface was equated to the low surface tension of PTFE. The smoothness surface due to the lower molding shrinkage and low polarity of the fillers were taken into explanation.

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CHAPTER VII

CONCLUSIONS

The 2^k factorial design of experiment (DOE) was used as the primary analysis to determine the effect the blending parameters. The main and prime parameters in the HDPE/PTFE blending process include the content of PTFE, Silane and DCP. DOE approach reviewed that the DCP content (-**C**) and interaction amount between PTFE and silane (**-AB**) used for manufacturing of HDPE/PTFE blend had negatively and significantly affected to the flow index of the HDPE/PTFE blend. While, DCP content was negative and significant effect (-**C**) to the flexural strength of the original blend samples. On the other hand, all of assigned parameters and their levels do not have the significant effect to the flexural strength of the HDPE/PTFE blends underwent sauna treatment. For the flexural modulus of HDPE/PTFE blends, the DCP (-**C**) and silane/PTFE (-**AB**) were the significant variable to the property of the original samples. Especially, the DCP (-**C**) was the negative and significant influence to the flexural modulus of the cured samples. The given designed experimental parameters and their levels used in this study did not have the real significant effect on the tensile properties of the original and sauna cured HDPE/PTFE blend. It was also found that DCP, PTFE and silane contents had no significant effect to the notched impact strength of HDPE/PTFE blends regardless to the samples conditioning. DCP, silane, PTPE contents did not have significant effect to the HDT of the blends. Both original and cured HDPE/PTFE blend samples, the surface tension, by mean of the ratio between the water drop diameter ratios, suggested that the parameters and their levels of content used in the blend ingredient had no statistical significant effect to the film surface of the blends. Finally, the results concluded that the parameters and their levels used for blending HDPE/PTFE had no influence to the wear property of the HDPE/PTFE blend films.

For the study of the effect of silane content in HDPE/PTFE blend, it was concluded that increasing the silane ratio of silane/DCP crosslink system added into the HDPE/PTFE blends, the MFI of the blends did not increase with increasing the silane coupling agent. HDT of the original samples were decreased with increasing the silane loading but after undergoing the sauna treatment the HDT was slightly increased with increasing the silane addition. However, at the given amount of silane, the HDT of the cured sample was significantly higher than the original sample. For the mechanical properties of HDPE/PTFE, the results were reviewed that that more flexible material, or softer, were found when increasing in the silane to DCP ratios. The tensile properties were also trend to decrease with increasing the amount of the silane. On the other hand, the impact strength of the blends was higher, softer material, when the silane used was increased. The dilution effects from the liquid silane were taken into the explanation for the mechanical properties dependency of the silane. The surface tensions of the film samples did not depend on the amount of silane added. The surface tension, investigated by the water drop ratio, was almost constant for all samples. The superior in the wear of the samples was found after the sauna treatment at 65°C for more than 12 hours.

For the effect of temperature on the surface treatment of PTFE by free radical decomposed from DCP before blending with HDPE, the results concluded that treatment temperatures of PTFE did not have the significant effect on the mechanical properties what so ever on the HDPE/PTFE blend. However, according to the investigation, the surface of PTFE was noticed to be enhanced when comparing with the surface of PTFE without the treatment. Better in the interfacial adhesion between HDPE matrix and treated PTFE were evidenced.

The addition of UHMWPE into the HDPE/PTFE blend as toughener was conducted. The results concluded that at higher UHMWPE content, above 5 phr with respect to the HDPE matrix, the mechanical properties especially flexural and tensile were decreased with increasing the UHMWPE contents. However, the impact strength was increased with increasing the UHMWPE addition. The increasing in the melt viscosity by adding the UHMWPE and hence retarding the melt mixing for the added ingredient was taken into explanation for the diminishing in the flexural and tensile properties and minor increase in the impact strengths of the HDPE/PTFE/UHMWPE blends. The trade-off between toughness improvements of the HDPE/UHMWPE blend matrix, high melt viscosity of the blend matrix and, consequently, poor dispersion and insufficient adhesion between PTFE and the blend matrix must be taken into consideration for the blending purpose. General speaking, the negative effect derived from adhesion was dominated over the toughness of the blend matrix especially at the high UHMWPE content.

The ability for the added UHMWPE powder to be fused with HDPE matrix was clarified. The effect of HDPE/UHMWPE master batching temperatures was resolved. It was manifested that better dispersion of UHMWPE was obtained by blending HDPE with UHMWPE by using UHMWPE/HDPE master batch pellet. UHMWPE was fused with HDPE matrix phase by direct powder blending but relatively poor dispersion was observed. Consequently, incompetency in the toughness would be occurred. The final properties of the HDPE/UHMWPE blends using the HDPE/UHMWPE master batch form concluded that there was no significant effect of the UHMWPE/HDPE master batching temperatures at 200^{o}C, 240^{o}C and 280^{o}C. The fusion and also dispersion of the UHMWPE within the HDPE matrix in the final blends were relatively similar. Consequently, there were no major differences in the properties of the HDPE/UHMWPE blend.

The fire clay powder and the combined talc/fire clay filler were tested as the fillers to investigate their influence on the flow ability, mechanical and also surface properties of the HDPE blend compound. By using only fire clay as filler, it was fond that the MFI of the fire clay filled HDPE/PTFE/UHMWPE composite was increased, lower in the melt viscosity of the composite. Fire clay filler acted as the lubricator type of filler. The mechanical and thermal properties of the composite material were slightly increased with increasing the fire clay loading. However, the fracture toughness of the composite material was deceased. The adhesion between the filler and polymer matrix was taken for the explanation. By using combined fillers between fire clay /talc fillers in the HDPE/PTFE/UHMWPE composite, it was found that the flow index of the composite did not increased by increasing the fire clay fraction. It was also found that the fire clay filler did not have the significant effect on the HDT of the composite. Moreover, the mechanical properties by mean of tensile and flexural were also slightly inferior when high portion of fire clay was added. The impact toughness was slightly increased with increasing the fire clay ratio. The surface properties both wear and tension were not obviously affected by the fire clay filler. The larger particle size of the fire clay than the talc was taken into explanation.

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APPENDIX A

PUBLICATION

Publication

Chantanakorn, N., and Meekum, U. (2012). Effect of Silane and UHMWPE content on the crosslinked HDPE/PTFE blends. In **Proceedings of the Polymer Processing Society 28th** (pp. 284). December 11-15, 2012, Pattaya, Thailand.

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EFFECT OF SILANE AND UHMWPE ON THE CROSSLINKED HDPE/PTFE BLENDS

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Abstract The peroxide initiated vinyl silane and moisture induced crosslinked HDPE/PTFE and HDPE/PTFE/UHMWPE were studied. The effects of silane contents at 2.0, 2.5, 3.0, 3.5 and 4 phr on the properties of the HDPE/PTFE blends were investigated. The contents of UHMWPE added on the HDPE/PTFE blends were also extendedly explored. Blending was manufactured on the co-rotation twin screw mixer. The standard test methods both mechanical and surface characteristics were employed. It was found that impact strength was increased with increasing the silane usage. Vice versa, MFI, flexural, HDT, surface properties of the blends were decreased with increasing the silane. Increasing in the network density via the silane/moisture condensation was the hypothesized explanation. At the given amount of silane, 4 phr, the HDPE/PTFE/UHMWPE having UHMWPE from 5 to 25 phr manifested that the MFI, tensile, HDT, flexural and the % wt loss were decreased with increasing the UHMWPE content. The notched impact and diameter of water drop ratio, however, slightly increased with the addition of the UHMWPE. The phase separation via adding the high molecular mass polymer into the blend was confirmed by SEM. The observation was used to explain properties incompetency of the UHMWPE for toughening the crosslinked HDPE/PTFE blends.

Keywords: Crosslinked HDPE/PTFE blend, HDPE/PTFE /UHMWPE blend, Mechanical properties and Surface characteristic.

Introduction

Contribution of the outstanding wear properties of PTFE in the polymer blends have been explored by the number of researchers. PEEK/PTFE blend indicated that the coefficient of friction in wear modes decreased with increasing the PTFE contents. At 30% of PTFE, the blend showed excellent combination of friction coefficient[1]. On the other hand, PEEK filled PTFE composite investigation showed that the lowest average friction coefficient($\overline{\mu}$) was obtained in the samples having PEEK at 50%(w/w). The lowest wear rate was obtained at 32% of PEEK filled sample[3]. Adding potassium titanate whiskers(PTW) into PEEK/PTFE composites seen that the PTW enhanced properties of the composite[4]. The blend between HDPE/UHMWPE was also published and found that the volumetric loss of the blends decreased with increasing the UHMWPE and it showed good mechanical properties[2]. Effects of untreated and pretreated carbon nanofibers(CNFs) on friction behavior and mechanical properties of UHMWPE/HDPE nanocomposites were also explored[5]. The enhancement in tensile strength of nanocomposites containing 0.5% of treated CNFs was four times higher than the untreated composite and pure sample. In this published work, the blend between HDPE/PTFE/UHMWPE was explored. The silane/peroxide crosslink system was added into the blends to enhance the compatibility and also mechanical inter lock via the chain networking formed. Main research objective was to obtain the blend material having the low surface adhesion characteristic.

Experimental

A. Materials

HDPE, H5814J, available from SCG-Chemical was used as the main polymer matrix. PTFE, Zonyl® MP 1300 and UHMWPE, UH 900, were purchased from DuPont and Asahi Kasei Sunfine and used as dispersed phase. Silane, Silquest® A-171, the vinyltrimethoxy silane(VTMS) with dicumyl peroxide(DCP) was used as crosslink system.

B. Sample preparation

For the HDPE/PTFE blends, PTFE was pretreated with 0.5 phr of DCP and 1 phr of silane in internal mixer at 100°C. Solution of 2.0, 2.5, 3.0, 3.5 and 4.0 phr of silane with 1 phr of DCP and dried HDPE pelltet were brought into cooperating and rigorously checked, respectively. Then, 20 phr of silane treated PTFE was added into the solid mixture and vigorously mixed. The solid ingredient was fed into twin screw extruder. The melt compounding was performed at screw speed of 10 rpm and constantly the barrel temperature at 190°C. The compound strand was cooled down and pelletized. The compound formula are shown in Table 1.

In order to study the effect of UHMWPE content in HDPE/PTFE blends, the master batch of UHMWPE at 60 phr in HDPE were manufactured at 200°C in twin screw mixer. The calculated amount of UHMWPE at 5, 10, 15, 20 and 25 phr, respectively, was added into the blend and compounded in the same manner as described in HDPE/PTFE blend. The designed compound ingredients of HDPE/PTFE/UHMWE are given in Table 2.

Table 1 Composition of the HDPE/PTFE blends with different silane content

Sample No.	HDPE (g)	PTFE (g) (phr)	DCP (g) (phr)	Silane (g) (phr)
HDPE/PTFE#1	400	80(20)	4(1)	8(2.0)
HDPE/PTFE#2	400	80(20)	4(1)	10(2.5)
HDPE/PTFE#3	400	80(20)	4(1)	12(3.0)
HDPE/PTFE#4	400	80(20)	4(1)	14(3.5)
HDPE/PTFE#5	400	80(20)	4(1)	16(4.0)

Table 2 Composition of the HDPE/PTFE/UHMWPE blends

Sample No.	HDPE(g)	PTFE (g) (phr)	DCP (g) (phr)	Silane (g) (phr)	UHMWPE (g) (phr)
HDPE/PTFE/UH#1	400	80(20)	4(1)	16(4)	20(5)
HDPE/PTFE/UH#2	400	80(20)	4(1)	16(4)	40(10)
HDPE/PTFE/UH#3	400	80(20)	4(1)	16(4)	60(15)
HDPE/PTFE/UH#4	400	80(20)	4(1)	16(4)	80(20)
HDPE/PTFE/UH#5	400	80(20)	4(1)	16(4)	100(25)

C. *Material testing*

The injection molding specimen was achieved at 190°C, 200°C, 210°C and 220°C from feed to nozzle, respectively and mold temperature of 30°C. Film samples with thickness of approx. 0.4 mm were fabricated by compression at 200°C and used for wear and liquid surface tension. Both samples were divided into 2 sets; annealed at room temperature and sauna cured at 65°C. Performance testing; tensile, flexural, impact testing, HDT and wear resistance were performed in accordance with the ASTM standards The liquid surface tension investigation was calculated from the micro drop, 1 µl, of distilled water(d_s) on the sample surface divided by the water diameter on referee material, PTFE sheet, (d_R).

Results and Discussion

A. Physical Properties

The effects of silane contents on the mechanical properties of HDPE/PTFE blends are summarized in table 3 to table 5, respectively. Generally, it is seen that the properties of the blends is fractionally increased via the sauna incubation. There might be two folds explanation, crosslinking via silane/moisture condensation and increasing in the crystallinity during the annealing process. From the results presented, the tensile properties seem to be independence on the silane contents. However, the flexural properties are lowered with increasing the contents. Implying that the materials had low in bending toughness. On the other hand, impact strength is marginally increased with increasing the silane content. Without the flow ability data, it might say that the increasing in crosslink density of the blends is suspected. Therefore, the material becomes more brittle. Nevertheless, from the MFI and HDT results shown in table 6, it is seen that the index does not obviously change with the silane addition. Consequently, the network density of the chain does not increase as expected. Another point of consideration could be taken into account is the interfacial bonding between polymer matrix and PTFE particle. This evidence will be presented by SEM data. For HDT outcome, it is observed that the HDT is decreased with increasing the silane for the original samples but it tendency to be increased after the sauna curing. Again, gaining the crystallinity via thermal prolonging would be the main reason.

Table 3 Tensile properties of HDPE/PTFE blends

Sample No.	Tensile strength(MPa)		Tensile modulus (GPa)	
	Original	Cured	Original	Cured
HDPE/PTFE#1	22.11±0.47	23.36±0.45	0.78±0.01	0.82±0.05
HDPE/PTFE#2	22.52±0.32	23.14±0.41	0.79±0.06	0.76±0.06
HDPE/PTFE#3	22.62±0.21	22.86±0.65	0.76±0.11	0.83±0.06
HDPE/PTFE#4	22.66±0.11	22.40±0.71	0.79±0.05	0.73±0.13
HDPE/PTFE#5	22.66±0.26	21.60±0.42	0.76±0.07	0.67±0.05

Table 4 Flexural properties of HDPE/PTFE blends

Sample No.	D_{sample} /D_{PTFE}		Weight loss (%)	
	Original	Cured	Original	Cured
HDPE/PTFE#1	1.03±0.09	1.01±0.08	0.56±0.02	0.25±0.03
HDPE/PTFE#2	1.03±0.11	1.01±0.02	0.48±0.02	0.25±0.02
HDPE/PTFE#3	1.04±0.05	1.00±0.12	0.48±0.05	0.23±0.05
HDPE/PTFE#4	1.04±0.05	0.98±0.24	0.41±0.06	0.18±0.03
HDPE/PTFE#5	1.04±0.04	0.96±0.07	0.40±0.08	0.11±0.03

Table 5 Impact strengths of HDPE/PTFE blends

Sample No.	Notched (kJ/m^2)		Unnotched (kJ/m^2)	
	Original	Cured	Original	Cured
HDPE/PTFE#1	4.01±0.25	4.18±0.18	NB	NB
HDPE/PTFE#2	4.02±0.21	4.49±0.21	NB	NB
HDPE/PTFE#3	4.35±0.13	4.77±0.19	NB	NB
HDPE/PTFE#4	4.43±0.14	4.99±0.25	NB	NB
HDPE/PTFE#5	4.46±0.11	5.04±0.07	NB	NB

Table 6 MFI and HDT of HDPE/PTFE blends

Sample No.	MFI@200/5.00 (g/10min)	HDT (oC)	
		Original	Cured
HDPE/PTFE#1	0.422±0.034	67.8±2.5	74.9±2.7
HDPE/PTFE#2	0.422±0.015	66.3±2.3	75.5±0.6
HDPE/PTFE#3	0.422±0.016	66.2±1.3	78.5±0.5
HDPE/PTFE#4	0.422±0.020	64.1±1.4	79.3±1.6
HDPE/PTFE#5	0.421±0.032	64.1±0.4	79.3±0.1

The mechanical properties of HDPE/PTFE/UHMWPE blends are shown in table 7 to table 9. Incorporating 5 to 25 phr of UHMWPE into the HDPE/PTFE blends. Again, it is seen that sauna curing has obvious positive effect to the properties. The tensile and flexural properties are slowly decreased with increasing the UHMWPE loading both original and cured samples. The phase separation between UHMWPE particle and the matrix due to the insufficient fusion energy of the high molecular weight polymer during the mixing process is explained. Recalling that, only 190°C mixing temperature was employed, compared with above 300°C of the UHMWPE processing temperature. Consequently, the ultra high mass polymer would only aggregate into the matrix phase. The toughening process could not be achieved. Vice versa, the impact strengths of the tertiary blends is raised by adding more of UHMWPE. It indicates that UHMWPE particles are acted as the crake energy absorber. Hence, they inhibit the crake growth. Flow ability and thermal properties of the blends are given in table 10. As expect, it is seen that the flow index of the blend is reversely affected by the ultra high polymer content. But the HDT is lowered by adding more UHMWPE for both original and cured samples. It is because UHMWPE has lower in HDT than the blend matrix.

Table 7 Tensile properties of HDPE/PTFE/UHMWPE blends

Sample No.	Tensile strength(MPa)		Tensile modulus (GPa)	
	Original	Cured	Original	Cured
HDPE/PTFE/UH#1	22.66±0.26	21.60±0.42	0.76±0.07	0.67±0.05
HDPE/PTFE/UH#2	19.44±0.91	20.12±0.16	1.33±0.11	0.71±0.02
HDPE/PTFE/UH#3	18.88±0.46	19.90±0.48	1.27±0.02	0.71±0.02
HDPE/PTFE/UH#4	18.71±0.57	19.49±0.23	0.98±0.38	0.68±0.03
HDPE/PTFE/UH#5	18.71±0.27	19.39±0.52	0.66±0.05	0.68±0.03
HDPE/PTFE/UH#6	18.66±0.46	19.34±0.33	0.63±0.02	0.68±0.04

Table 8 Flexural properties of HDPE/PTFE/UHMWPE blends

Sample No.	Flexural strength(MPa)		Fluxuralmodulus(GPa)	
	Original	Cured	Original	Cured
HDPE/PTFE/UH#1	36.68±0.99	38.16±1.30	1.91±0.16	2.03±0.09
HDPE/PTFE/UH#2	25.59±1.27	29.98±1.17	1.25±0.08	1.47±0.09
HDPE/PTFE/UH#3	25.02±1.03	29.54±0.67	1.23±0.08	1.47±0.05
HDPE/PTFE/UH#4	24.62±0.42	29.49±0.60	1.20±0.03	1.47±0.05
HDPE/PTFE/UH#5	25.96±0.79	29.31±0.17	1.24±0.04	1.46±0.01
HDPE/PTFE/UH#6	25.52±0.32	28.93±0.75	1.21±0.02	1.46±0.04

Table 9 Impact strength of HDPE/PTFE/UHMWPE blends

Sample No.	Notched (kJ/m^2)		Unnotched (kJ/m^2)	
	Original	Cured	Original	Cured
HDPE/PTFE/UH#1	4.46±0.11	5.04±0.07	NB	NB
HDPE/PTFE/UH#2	6.02±0.23	6.60±0.23	NB	NB
HDPE/PTFE/UH#3	6.41±0.11	6.80±0.15	NB	NB
HDPE/PTFE/UH#4	6.89±0.30	7.24±0.23	NB	NB
HDPE/PTFE/UH#5	7.22±0.04	7.64±0.22	NB	NB
HDPE/PTFE/UH#6	7.49±0.08	7.52±0.18	NB	NB

Table 10 MFI and HDT of HDPE/PTFE/UHMWPE blends

Sample No.	MFI@200/5.00 (g/10min)	HDT (°C)	
		Original	Cured
HDPE/PTFE/UH#1	0.421±0.032	64.1±0.4	79.3±0.1
HDPE/PTFE/UH#2	0.031±0.031	62.8±2.6	77.9±1.8
HDPE/PTFE/UH#3	0.031±0.021	58.9±0.6	76.9±0.1
HDPE/PTFE/UH#4	0.022±0.063	58.1±0.6	75.3±1.9
HDPE/PTFE/UH#5	0.021±0.012	57.3±0.3	75.3±0.9
HDPE/PTFE/UH#6	0.019±0.012	57.2±0.4	75.2±1.8

B. Surface Characteristics

The surface properties of HDPE/PTFE blends with against the silane loading by mean of water drop ratio and wear test are summarized in table 11. It is found that water diameter ratio and % wt loss are decreased when increasing the silane content. It also notices that the sauna annealing lower the tests values, especially the wear test. Deceasing in the diameter of water drop ratio means the lower in surface tension of the blends. Similarly, decreasing in % wt loss indicates the surface friction or good adhesion between PTFE particle and matrix. From the results, it suggest that the surface tension and wear properties of the blend is improved by adding more silane coupling agent. Table 12 presents the surface characteristic of HDPE/PTFE/UHMWPE blends. In contrast with the HDPE/PTFE blends, the water drop ratio and wear properties of the blends do not enhance by incorporating the UHMWPE. Moreover, the surface tension has tendency to be inferior by adding the polymer. It indicates that phase separation of UHMWPE due to the insufficient fusion energy would have the significant and negative effect to the surface properties of the blends. This evidence will be concluded by the SEM analysis later on.

Table 11 Surface characteristic of HDPE/PTFE blends

Sample No.	D_{sample}/D_{PTFE}		Weight loss (%)	
	Original	Cured	Original	Cured
HDPE/PTFE#1	1.03±0.09	1.01±0.08	0.56±0.02	0.25±0.03
HDPE/PTFE#2	1.03±0.11	1.01±0.02	0.48±0.02	0.25±0.02
HDPE/PTFE#3	1.04±0.05	1.00±0.12	0.48±0.05	0.23±0.05
HDPE/PTFE#4	1.04±0.05	0.98±0.24	0.41±0.06	0.18±0.03
HDPE/PTFE#5	1.04±0.04	0.96±0.07	0.40±0.08	0.11±0.03

Table 12 Surface characteristic of HDPE/PTFE/UHMWPE blends

Sample No.	D_{sample}/D_{PTFE}		Weight loss (%)	
	Original	Cured	Original	Cured
HDPE/PTFE/UH#1	1.03±0.42	0.96±0.07	0.49±0.07	0.40±0.03
HDPE/PTFE/UH#2	1.03±0.07	0.90±0.01	0.49±0.17	0.39±0.16
HDPE/PTFE/UH#3	1.03±0.06	0.90±0.05	0.49±0.16	0.38±0.17
HDPE/PTFE/UH#4	1.03±0.05	0.99±0.11	0.49±0.21	0.38±0.14
HDPE/PTFE/UH#5	1.05±0.09	1.04±0.04	0.49±0.03	0.37±0.24
HDPE/PTFE/UH#6	1.05±0.02	1.04±0.06	0.44±0.04	0.35±0.21

C. Morphology of Blends

SEM micrographs at X1000 of HDPE/PTFE blends with 2.0, 3.0 and 4.0 phr of silane are displayed in Figure 1**(a)** and 1**(b)** for original and cured, respectively. It is obviously seen that the PTFE particle is dispersed on the HDPE matrix. The PTFE pull out is the major crake phenomenon. According to the morphological observation, increasing in the silane contents do not manifest any vast improvement of the adhesion between the particle and the matrix. This indication could be used to explain why the tensile and flexural properties of the HDPE/PTFE blends do not superior by increasing the silane content as described earlier.

Closer investigation of the fractured surface, it is seen that the web like traces at the matrix, HDPE, is more obvious after sample undergo sauna incubation. Also, the number of webs do seemingly and directly depend on the amount of silane used.

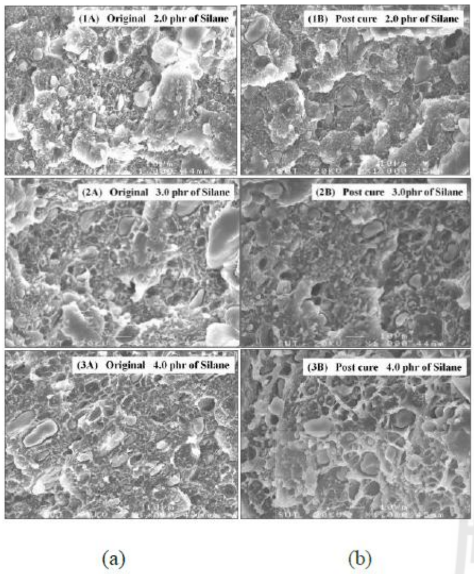

Figure 1. SEM photographs of HDPE/PTFE blends with 2.0, 3.0 and 4.0 phr of silane both, (a) Original and (b) sauna cured samples, respectively.

The web like traces could be resulted from the silane/moisture crosslink reaction. The network density would increase with increasing the silane addition.

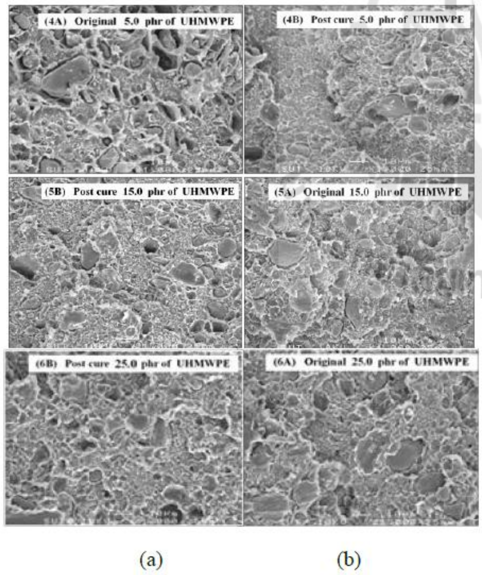

Figure 2. SEM photographs of HDPE/PTFE/ UHMWPE blends; (a) Original and (b) cured sample.

Figure 2 is the SEM photographs of the HDPE/PTFE/UHMWPE blends at 5, 15 and 25 phr of UHMWPE with and without sauna curing, respectively. It does quit obvious to see that the UHMWPE particles are separated and dispersed on the HDPE matrix. This unmelted high molar mass chain would cause the inferior in the tensile and flexural properties of the blends. As mention before, the sauna incubation do not assist the adhesion between the dispersed particles but it promotes the crystallinity and the network formation via silane/moisture induced reaction at the matrix phase. Therefore, the cured process does not have much of the positive effect on the mechanical properties of the HDPE/PTFE/ UHMWPE blends as presented early on.

Conclusions

Increasing the silane in the HDPE/PTFE blend system found that the mechanical properties, tensile and flexural, are decreased. The increasing in the network formation via increasing the silane content were taken into explanation. The silane did not improve the adhesion between HDPE matrix and PTFE dispersed phase. In the tertiary blend system, HDPE/PTFE/ UHMWPE, it was found that the mechanical properties were also depleted at higher UHMWPE loading. The phase separation of unmelted UHMWPE particle was played the important role for the inferiority.

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BIOGRAPHY

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